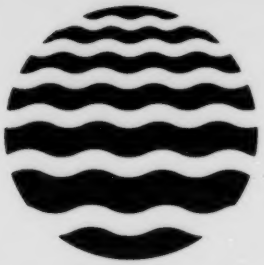
STOPPING WATER POLLUTION AT ITS SOURCE



MISA

Municipal/Industrial Strategy for Abatement

Kraft Mill Effluents in Ontario

Date:	April 1988
Prepared by:	Norman Bonsor, Neil McCubbin and John B. Sprague
For:	Environment Ontario

LIST OF ERRATA

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by the Expert Committee on Kraft Mill Toxicity,
for the Pulp and Paper Sector of MISA,
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Report prepared for the Technical Advisory Committee,
Pulp and Paper Sector of MISA
Ontario Ministry of the Environment
Toronto, Ontario, Canada

by

the Expert Committee on Kraft Mill Toxicity, 29th March 1988

Norman Bonsor
Dept. of Economics
Lakehead University
Thunder Bay, Ontario
P7B 5E1

Neil McCubbin, Eng.
Consulting Engineer
140 Fisher's Point
Foster, Quebec
J0E 1R0

John B. Sprague
Dept. of Zoology
University of Guelph
Guelph, Ontario
N1G 2W1

c 1988 Her Majesty the Queen in right of Ontario as represented by the Minister of the Environment

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1. SUMMARY

> *"The cost of pollution abatement is a cost of doing business"*
> *J.R. Kimberly, former President of Kimberly-Clark Corporation (Billings and Narum 1966)*

> "We recognise the urgent need for environmental control expenditures, but we also recognise an equally urgent need to improve our cost competitiveness with producers in the US...."
> *Abitibi-Price Inc Annual Report, 1976, p3*

The foregoing quotations symbolise the current background to environmental protection in the pulp and paper industry. Industry accepts the principle that protection of the environment is a necessary cost of doing business, but has been reluctant to put the principle into practice. In the absence of equitable and uniformly enforced environmental regulations, industry cannot be expected to commit resources to environmental protection.

The challenge facing regulatory authorities is that of formulating and implementing an environmental protection policy which is ecologically effective, enforceable, politically acceptable and economically viable. Industry managers must be able to fulfil environmental goals in a cost effective manner in order to survive.

1.1 Overview

This report reviews the effluent discharged by the kraft pulp industry in Ontario, and recommends a water pollution control strategy. The recommendations are based on the needs of the aquatic ecosystem, current technology, water pollution control practices in other kraft pulp producing jurisdictions, and economic factors.

This report was prepared for the Joint Technical Committee, Pulp and Paper Sector, MISA by the "Expert Committee on Kraft Mill Toxicity", consisting of the three authors, who are independent of the pulp industry and the Ministry of the Environment. The content represents the considered opinions of the authors, who are jointly responsible for its contents.

Criteria for four levels of environmental protection are presented, along with the economic costs implied by each. We consider that it is the government's responsibility to select the most appropriate level or levels, and to define the time schedule, but have included some suggestions in the body of the report. The costs of attaining the third level of achievement would be small for most Ontario mills, and this level of environmental protection could be accomplished in a few years. **The cost of realising the fourth level of achievement would be much higher.** We suggest that the time frame for reaching level IV be set at five years or more, in view of the complexity of the multiple changes which would be required in bleach plants, and to allow for research to develop better means of attaining or even exceeding this high level of environmental protection.

The recommendations maintain the standards set by the traditional regulations on fish toxicity and other parameters. They also include controls on organochlorines,[1] some shift in emphasis from BOD as a

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1 Organochlorines, chlorine bound to various organic molecules, are members of a very large family of substances found in many waste waters, including those discharged by bleached kraft mills. The "dioxins" frequently mentioned in the media are a tiny but notorious proportion of the organochlorines.

control parameter toward persistent substances, additions to the traditional fish toxicity test and suggestions for research in improving knowledge of environmental control technology.

The recommendations represent a departure from recent regulatory philosophy in both substance and practice. We do not believe that the regulations introduced over the past two decades have been successfully enforced. Nor do we feel that those regulations are entirely appropriate for Ontario kraft mills as we prepare to enter the 1990's. They have been used as a catch-all for a diverse range of pollutants. To-day's technology offers approaches which are more efficient in securing overall protection of the environment. Our approach fits the general concepts of the MISA program in as much as it (a) emphasizes the control of **persistent toxicants**, (b) is based on proven and **available technology**, and (c) is site specific in many respects, the protect the **water quality** at individual locations.

We have reviewed the available information on organochlorines, including the dioxins which have received so much media attention. We have concluded that it is desirable to reduce the quantities of organochlorines discharged from kraft mills. We consider that the chlorinated dioxins do not represent an immediate danger to human health and welfare, but that in a few locations downstream of kraft mills the possibility exists of heavy fish-eaters consuming more than the acceptable daily intake of 2378 TCDD.

In the long run, **the goal should be to completely eliminate the formation of organochlorines** . This would probably imply the elimination of chlorine and chlorine compounds as reagents for bleaching kraft pulp. There is no current technology proven on an industrial scale which is capable of producing highly bleached kraft pulp without the use of at least some chlorine.[2] Accordingly, we have based our recommendations on limitation of organochlorine discharges on existing technology rather than on levels in the receiving water.

We have recommended regulations for maintaining **dissolved oxygen concentrations** in the receiving waters, which will limit BOD discharges for mills on smaller receiving waters to quite low levels, with an absolute maximum discharge which corresponds to the Canadian Federal guideline of 30 kg/tonne pulp.

The traditional test of **non-lethality of an effluent for rainbow trout is maintained** at the original level of stringency by specifying a fixed allowance for water use per unit of pulp production, so that the total amount of toxic substances released is more effectively controlled than it has been in the past. We also recommend regulations requiring that there will be **no sublethal effects (growth, reproduction) on aquatic organisms at the edge of a mixing zone around the mill effluent outfall.**

We have discussed options for improving the quality of kraft mill effluent in order to show that feasible technical solutions exist. These serve as the basis for the economic analysis. There are several potential solutions for each mill, and we consider that **pulp producers should be totally responsible for selection of the technology to be used to comply with whatever regulations the Minister may develop as a result of this report,** in keeping with the stated approach of MISA.

We do not support the concept of "Best Available Technology" of effluent control for the kraft pulp industry, insofar as many people have the impression that this would require secondary treatment at all mills. In some cases that may not be environmentally necessary. Instead we support those in-plant controls and

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2 There have been some promising laboratory demonstrations of such technology, and we urge that these be pursued to the pilot plant level as soon as possible.

process modifications, which we believe to be more desirable environmentally and economically, particularly in the long term.

The report strongly suggests that the multi-chemical approach used in MISA for assessing toxic discharges as part of the "water quality track" is not appropriate for the kraft pulp industry. We consider that it is overly expensive and probably doomed to failure because of its inherent complexity.

1.2 Recommendations

The recommendations of the Committee are summarised below, with a very brief explanation of the rationale behind them. Detailed discussions of the technology and economics, including the literature references, are included in the body of the report. The intent of these recommendations is to assist the Ministry in formulating a policy and writing regulations which will be fair, effective in protecting the environment, enforceable, and economically attainable by the Ontario kraft industry given the competitive nature of world markets.

1.2.1 Recommended Goals

Mills should reach one of the following alternative levels of achievement, as selected by the Ministry.

Table 1.1 Levels of achievement for kraft component of pulp and paper mill effluents.

Level	BOD kg/ADt	SS kg/ADt	Site-specific DO in receiving-water outside mixing zone (NAS/NAE 1974) Refer to Sect. 11	Lethality of effluent for standard discharge volume of 175 m^3/t pulp	Sublethal toxic effect beyond the mixing zone	Organochlorines kg TOX/ADt
I	>30	>15	DO is at low level of protection or worse	LC50 < 50%	yes	≥5.0
II	<30/16.5	<15	DO meets low level but not moderate level of protection	LC50 > 50%	yes	<4.5
III	<30/16.5	<10	DO meets moderate level of protection	LC50 ≥ 100%	none	<2.5
IV	<30/16.5	<10	DO meets high level of protection	LC50 ≥ 100%	none	<1.5

Within one mill there may be uneven levels of control for the different characteristics of the waste. For example, there could be excellent control of suspended solids but an unsatisfactory level of toxicity. Such qualities may be rated independently for "level of achievement", again indicating where the focus should be for improvements.

Economic costs have been assigned to each of the four levels of achievement in order that the social and economic factors may be considered alongside the environmental ones. The levels of achievement range from what we consider to be unsatisfactory to very satisfactory. The choice of which level or levels are most appropriate is a political one.

The four levels should be utilised to set a time-frame for future improvements, with due consideration of the technical and economic feasibility of the necessary mill modifications and the practical limits on time required for engineering and construction of major process equipment.

All levels of achievement can be attained with current industrially proven technology. Levels II and III can be achieved fairly rapidly and in most cases with little real cost. However, neither Level II nor Level III could be achieved instantaneously by any given mill, since process changes would have to be phased in. One to three years is an attainable time scale for engineering, equipment procurement, installation and commissioning of appropriate facilities, all of which are available from established competitive capital equipment suppliers.

Level IV is also attainable with currently proven technology, but in almost all mills considerable expense would be involved in attaining the organochlorine limit. Level IV TOX should be a goal for around 1993, and during that period research may develop new and more economical ways of reducing the discharges of organochlorines

The requirements for BOD and SS conform with current Ontario requirements. The minimum levels of dissolved oxygen required by column 4 might best be underctood by an example. If the normal summertime concentration of dissolved oxygen in the receiving water were 9 mg/L, Level I would require a minimum of 4 mg/L in the same summer conditions, Level II would be 4.5 mg/L, Level III would be 6.2 mg/L, and Level IV would require a minimum of 7.7 mg/L

The toxicity criterion is the same for Levels III and IV, since there is no way of estimating an LC50 once it rises above 100% effluent concentration, and therefore no way of specifying a further improvement.

1.2.2 Establishing BOD Discharge Limits

The foregoing specifications of levels of achievement regulate BOD discharges directly according to the Federal standards for new mills. They also regulate BOD indirectly by defining acceptable dissolved oxygen concentrations in the receiving waters. It is recommended that for control orders the allowable BOD discharge be determined by calculating the appropriate value for worst case conditions, using assimilative capacity prediction technology, and that the mill be required to comply with this limit consistently, perhaps with seasonal modifications if appropriate. On-going stream or lake surveys will be desirable in most cases to monitor environmental quality and refine the estimates of acceptable BOD discharge.

1.2.3 BAT

The so called "Best Available Technology" approach to regulating effluent from kraft mills suffers from a serious practical weakness as a policy option for controlling effluent flows. At present the perception most industry and Ministry staff seem to have is that BAT would require all mills to install secondary treatment as a first step in improving effluent quality. We consider that, for some mills, this is not justified and would divert energies and finances away from more environmentally and economically beneficial in-plant measures for improving effluent quality.

The term "Best Available Technology" is all too often a misnomer since the technology implied is not the best in the minds of many professionals in the environmental field. The terms "BAT", "BPT" etc originated in the US as a result of legislation, tortuous negotiations and court battles, and have been transposed to Ontario, giving rise to some misleading conceptions which are neither technically sound nor environmentally useful in Ontario as we enter the 1990's. [3]

1.2.4 BOD vs Organochlorine

We recommend that as a general policy BOD not be treated as a "catch-all" for the discharge of organic wastes into surface water. Switching the emphasis to organochlorines (TOX) will provide a much better level of environmental protection by directly regulating the discharge of organochlorines. BOD remains useful, particularly when dissolved oxygen levels in the recipient are of concern. **Any measures implemented to reduce organochlorine discharges will also reduce emissions of traditional pollutants, and many of the substances that are included in the proposed MISA testing program.**

1.2.5 Organochlorine Discharges [4]

We recommend that the Ministry adopt a policy of regulating Total Organic Halogen discharges. The medium and long-run regulatory levels should be expressed on a per-tonne-of-kraft-pulp basis and should be the same for all kraft mills regardless of wood species and bleaching process used.

1.2.6 Chloroform

We recommend that the Minister investigate the chloroform concentrations in the ambient air around those kraft mills which use hypochlorite bleach and then determine what action is required.

1.2.7 Control Parameters for Toxicants

We recommend that the major quality parameter for persistent toxicants to be applied to effluent discharges in the Ontario kraft sector should be that of Total Organically bound Halogens (TOX.) **We**

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3 We recognise that some Ministry documents specify that BAT should be determined by analysis of the situation at each mill, and may include in-plant and/or external measures. However, if the BAT concept as defined in these documents is to be effectively implemented in Ontario, it will be essential to correct the above mentioned misconceptions about BAT.

4 Organochlorine is a generic name for chlorine that is attached to an organic chemical. Quantities and concentrations of these substances are usually expressed in terms of the mass of organically bound chlorine, as determined by one of several analytical protocols including TOCl, AOX and TOX. Much of the Scandinavian literature uses the term TOCl to signify organic chlorine.

recommend this generic approach for the kraft pulp industry in preference to the detailed approach envisaged under the MISA initiative of specifying discharge limits for a potentially large number of individual substances. Our rationale for recommending a generic criterion as opposed to MISA's large list of specific criteria is two-fold. First, only a small proportion of hundreds of specific substances in kraft mill effluent have been identified. Thus basing regulations on a list of specific substances is environmentally dangerous, and likely to lead to an ever increasing (and ineffective) list of regulated pollutants. Second, the establishment of protocols and actual testing for a potentially large number of substances is likely to be both time consuming and expensive for both government and industry. Technical and financial resources would be better directed towards securing reductions of discharges of deleterious substances.

1.2.8 Determination of Organochlorines

We recommend that the discharge of organochlorines be determined by either an analytical technique or a mathematical one, at the choice of each mill. The recommended analytical method is **Total Organic Halogen**, as defined in APHA et al. (1985) "Standard Methods", 16th Edition.[5]

It is recommended that the mathematical technique described by Germgård (1983), which is based on the quantities of chlorine and chlorine compounds used in the bleaching process, be accepted as a provisional expedient to overcome the temporary lack of data on TOX in Ontario kraft mills.

We recommend that implementation of regulations to limit discharges of organochlorines should not be delayed by an extensive debate over whether the control parameter should be TOCl, TOX, AOX, dioxin or other.

1.2.9 Organochlorines in Pulp

We recommend that Control Orders be worded to prohibit modification of the bleaching process either to export organochlorines with the pulp so as to improve effluent quality or to divert organochlorines to the effluent from the pulp to satisfy pulp quality criteria of purchasers. We have avoided recommending a regulation on organochlorine content of pulp, since there is presently no proven technology available to control the split between pulp and effluent. [6]

1.2.10 Research on Chlorine-free Bleaching

Research and development of chlorine-free bleaching sequences should be actively encouraged. Considerable laboratory work has indicated that elemental chlorine can be eliminated and other forms of chlorine reduced to zero or very low levels, but we have been unable to recommend regulations which would effectively mandate such technology as it is not proven on an industrial scale. Any mill willing to

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5 "Total Organic Halogen" is frequently abridged to "TOX", which is an unfortunate choice of letters due to the apparent connection with toxicity. In deference to common practice and the definition in APHA Standard Methods, we have used the abbreviation "TOX" throughout this report.

6 The purpose of this recommendation is to forestall any environmentally unsound practices which may be developed as a result of pressure from foreign regulatory or local authorities

install a pilot or full scale system of this nature should be actively supported by incorporating provisions in the control order which would protect the mill against unforeseen difficulties in pioneering work.

1.2.11 Selection of Appropriate Technology

The Ministry should not specify particular means of reaching a given effluent quality. **Mills should be free to select whatever technology they wish, providing that it will comply with effluent discharge limits,** and other regulations. For example, there are a number of proven ways for reducing organochlorine discharges and it should be up to individual mills to decide on how they are going to comply with the required level. Such an approach is repeatedly emphasised in MISA documents.

1.2.12 Toxicity Tests

We recommend that tests monitoring the toxicity of effluents from bleached kraft pulp mills be performed at a fixed maximum effluent flow of 175 m^3 per tonne of air-dried pulp produced, for the standard Ministry of the Environment static test of acute lethality to rainbow trout. The rationale for this is to encourage the mills towards economy of water consumption, which brings with it tighter control of mill processes and reduced loss of substances including persistent toxic chemicals, to the environment. The recommendation maintains the same toxicity control as was intended when the federal regulation was issued.

To re-emphasise, we consider that a **toxicity standard based on the concentration of the effluent** (as opposed to the mass flow of toxic substances) is **inappropriate for the kraft pulp industry, and discourages technical development and implementation of certain environmentally desirable technologies, such as oxygen delignification**, dry debarking and water conservation in general.

1.2.13 pH in Toxicity Tests

Toxicity tests for monitoring kraft mill effluent should be run at pH 7 or at the pH of the receiving water. The effect of pH should not be included in the toxicity test, since it is not a factor in the environment after mixing.

1.2.14 Rapid Toxicity Testing

The Ministry should encourage mills to obtain and use, one or other of the recently introduced methods for rapid toxicity testing based on reactions of bacteria. These would be helpful in finding and eliminating sources of toxicity, because of the ease of performing the tests, and the almost immediate feedback of results. The Ministry should recognise the appropriate test or tests as an acceptable way of routinely measuring and reporting toxicity.

1.2.15 Absence of Sublethal Effects

The Ministry should phase in a policy and regulations that require no overt sublethal effects of kraft mill effluent beyond the edge of a mixing zone. Compliance should be checked (yearly?) by laboratory tests

on growth of newly-hatched fathead minnows or reproduction of the water-flea *Ceriodaphnia* or both. The genotoxicity of effluents should also be tested, perhaps less frequently. Those results should be tied in with field surveys of dispersion and dilution, and biological effects in the surrounding aquatic communities.

The program should be actively led at a high level of management, so as to integrate the various groups of people involved, and to ensure that decisions are reached on whether sublethal effects are absent, and to ensure that action is taken if necessary.

Such a policy requires definition of mixing zones. That should be done on the basis of surface area affected, as recommended in the Hanna report to MISA.

1.2.16 Phosphorus

It is recommended that phosphorus discharges from mills be limited to the amount that enters with the wood and with the make-up chemicals, plus any nutrients that are essential to the efficient operation of a biological waste treatment system if one is installed. In most cases, this would simply require that mills use an alternative to phosphoric acid for cleaning process equipment.

1.2.17 Effluent Outfalls

It is recommended that mills be required to install effluent outfalls which eliminate foam, visible colour and other aesthetically undesirable environmental effects of their effluents, and provide the maximum dilution reasonably attainable in the receiving water. Most mills have already installed suitable diffuser outfalls. Calculations of the allowable BOD discharge should include the effect of the diffuser.

1.2.18 Spill Control

We recommend that control orders require mills to install an effective spill monitoring and alarm system, based on automatic sensors, and sufficient storage to minimise the risk of environmental damage due to human error or equipment failure.

Written instruction and **training** should be provided to mill operators and supervisors on using such systems.

Equipment should be installed and operational procedures implemented, to the maximum reasonable extent, so that no significant quantity of any of the following substances can spill to a biological treatment system or to the receiving water.

Black liquor
Soap
Petroleum products
Pulp stock
Lime mud

1.2.19 Control Orders

We recommend that Control Orders, or whatever other regulatory instruments are used to control effluent discharges, be issued for a **five year period**. This will provide a sufficient length of time for mills to plan and implement major changes required by the Ministry in terms of effluent quality. This does not imply that five years should be allowed for implementation of all the requirements of a control order. It is intended to ensure that industry should not be subjected to excessively frequent changes in the effluent quality requirements.

We feel that stable, progressive regulations are desirable to stimulate research and development, as well as the improved environmental awareness that mill employees must develop at the operating level to achieve optimum effluent quality.

1.3 Effluent Quality Criteria

There is no simple way of defining the quality of an effluent as "good" or "bad". Because of the wide variety of substances found in industrial effluents, and the wide range of receiving water characteristics, it is necessary to select a reasonable number of key criteria to provide a practical basis for protection of the environment by the normal legal and political process. These key criteria should be:

a) relevant to significant effects on the receiving waters;

b) measurable reliably and without excessive cost or elapsed time;

c) standardised among regulatory jurisdictions so that environmental technology can be transferred;

d) restricted in number so that sampling, analysis and enforcement costs are not unreasonable, and users of the data are not overwhelmed by its volume and complexity; and

e) comprehensible by anyone with a good general education so that the public may have confidence in the government and regulatory bodies.

In this respect, the committee is dismayed by the prevailing plans in the pulp and paper sector of MISA. The intention is to assess more than 100 substances over one year, at a cost which we estimate might be $400,000 per mill.[7] Further extensive testing is intended to follow, on a schedule which is not yet defined. We feel that such consumption of economic assets and technical expertise gains little in the case of kraft mills; instead we have listed recommendations for immediately embarking on a program of generic reduction of persistent pollutants. The following criteria are considered by the authors to be the most relevant to the protection of the environment from the undesirable effects of kraft pulp mill effluents.

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7 Estimate based on commercial rates for laboratory analysis, plus shipping, supervision, data analysis and reporting.

1.3.1 Biochemical Oxygen Demand (BOD)

BOD is a useful measure of the quantity of oxygen an effluent will demand from the receiving water and, by inference, the extent to which the effluent could lower the dissolved oxygen.

Three Ontario kraft mills have improved oxygen concentrations in the receiving water by secondary waste treatment. Some others do not have a problem because of in-plant controls, large volumes of receiving waters and effective diffusers on the outfall.

The effluents from the 9 Ontario kraft mills have a combined oxygen demand that is equivalent to the raw sewage of 1.4 million people, and the BOD of many of the effluents is as strong as raw sewage. Nevertheless that total deoxygenating potential is trivial in the overall budget of the most frequent recipient, Lake Superior, delicate as that lake is. Accordingly, we do not recommend any blanket requirement for secondary treatment for the purpose of reducing BOD.

It is technologically easy to promulgate regulations against BOD, and it would be easy to follow the US and require secondary treatment of all mill effluents. We do not suggest that approach. Instead we recommend stricter regulation as necessary to maintain favorable concentrations of dissolved oxygen in the particular local waterbodies at each mill-site.

BOD has been used in the past as an overall "catchall" for discharges of both deoxygenating and toxic substances, with some measure of success. We consider that in the case of the kraft pulp industry, control of persistent toxicants is better achieved by regulating organochlorines.

For both technical and conceptual reasons we are opposed to the "band-aid" approach of aerating the receiving water with oxygen, which was under consideration at one site.

1.3.2 Toxicity

Most kraft mill effluents with only primary treatment are lethal to fish. However these wastes are only mildly toxic and would not normally cause direct mortality after dilution in the environment. For the six Ontario kraft mills with only primary treatment, lethal concentrations typically ranged from 12% effluent to non-lethal, with wide variations between individual tests of each mill.

Secondary (biological) waste treatment may or may not render an effluent non-lethal. Of the three Ontario kraft mills with aerated lagoons, one has a consistently non-lethal effluent, but the other two mills, as of 1985 and 1986, had effluents that were as lethal as the average untreated effluent. Experience across Canada indicates that approximately half of the aerated lagoons discharge effluent which is non-toxic to fish, as defined by the Environment Canada test.

Sublethal toxicological effects on aquatic organisms are not specifically regulated in Ontario at present. From the results of extensive sublethal toxicological work with aquatic organisms exposed to kraft mill effluent, we consider that organisms would be protected from overt whole-organism effects if the maximum mill concentration in a waterbody were 10% of the LC50 for that effluent, and the average concentration were 5% or less of the LC50.

1.3.3 Organochlorines

A wide variety of chlorinated organic chemicals are formed in the kraft bleaching process, including chlorinated resin acids and chlorinated phenolics which can cause acute lethality to fish and the dioxins which have attracted so much attention in the media. However, the real cause for concern about organochlorines is the unknown degree to which highly toxic and persistent organochlorines are formed, and escape to the environment. (i.e. **it is a safe assumption that in time more environmentally undesirable substances will be discovered, just as unexpected as the chlorinated dioxins**).

The MISA program will address control of a few of the organochlorines, but since there are probably thousands of them, we question whether that part of MISA's approach which is based on a long list of specific compounds, can be effective. For the pulp industry, a broadly based definition of the undesirable substances (organochlorines) is more practical, such as the amount of **Total Organic Halogen** [8] **(TOX)** as defined by the analytical procedure of the American Public Health Association (APHA et al. 1985). We consider that high priority should be given to reducing discharges of organochlorines.

1.3.4 Nutrients

Phosphorous is the key nutrient in almost all fresh waters and algal production depends largely on phosphorus concentrations. We are most concerned about Lake Superior as a site of potential enrichment or eutrophication. Secondary waste treatment is of little or no benefit in reducing the outputs of nutrients, and in the case of kraft mills it may cause increases if phosphorus has to be added to the effluent to attain very high BOD reduction efficiency. Some of the phosphorus in kraft mill effluents originates in the wood used for pulping, or the lime purchased as make-up chemical in the recovery cycle, and its presence cannot be avoided. However, some phosphorus originates in the use of phosphoric acid and comparable chemicals for cleaning mill equipment and we have recommended that this practice be limited or other measures be taken to reduce phosphorus discharges.

1.3.5 Suspended Solids

Suspended solids were very significant pollutants in the discharge of mills prior to 1960, but they are now inconsequential in most mills in Ontario. All Ontario kraft mills have primary waste treatment to remove suspended solids from the effluents, and all mills are meeting provincial limits for discharge of suspended solids, except for one which is marginal. Discharges consist of fine particles of bark, wood fibre, and lime in the case of mills with only primary effluent treatment. Where a secondary treatment system is operating, the suspended solids are mostly biological matter. About 3 to 14 tonnes per day are discharged from the various mills. Although those are appreciable amounts, they are not causing significant problems.

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[8] The "X" refers to "Halogens", which are members of a family of chemical elements including chlorine. For all practical purposes "Organic Halogen" is equivalent to "Organic Chlorine" in the kraft pulp industry, since the other halogens are essentially absent.

1.4 Pulp Production and Economic Significance

There are 9 kraft pulp mills in Ontario producing approximately 2.3 million metric tonnes of pulp per year, which represents about 20% of Canadian kraft pulp production. The pulp and paper industry in Ontario ranks fifth in terms of contributing value added in the Province's manufacturing sector, and in 1984 accounted for 3.2% of total value added in manufacturing. The economic health of the industry is extremely important to the economy of northern Ontario. For a number of small communities, the pulp and paper industry is the major source of employment. Even in larger centres, the industry is a key part of the economic base.

The Ontario industry is reliant on world markets for the sale of a high proportion of its products and must therefore be highly efficient in terms of both cost and quality of its products.

1.5 Current Ontario Water Pollution Control Regulations

Kraft mill effluent quality in Ontario is regulated by issuing individual Control Orders to mills. These are negotiated individually, and typically cover a period of several years during which the mill owner is required to comply with certain limitations on effluent characteristics, and sometimes install additional environmental protection facilities or perform feasibility studies of potential environmental improvement measures.

There are also Federal regulations which apply to the Ontario kraft mills.

The effluent criteria which form the basis of the Control Orders issued to date have been suspended solids, BOD, toxicity, and nutrients.

1.6 Equivalent US and European Approaches

Environmental regulations for kraft pulp mills in the US are more stringent than those in Ontario. Specifications in the discharge permits are similar across the country but vary slightly from state to state. For the "conventional" pollutants, BOD and suspended solids, primary and secondary waste treatment is required to comply with US regulations. Specific toxic chemicals are also regulated by concentration.

Toxicity tests on the whole mill effluent have been specified in US discharge permits as they came up for renewal since the middle 1980s. Lethal and sublethal tests are often required on a fish, an invertebrate, and an alga. Usually it is required that at the edge of a mixing zone, the rare peak concentrations of effluent should not exceed one-third of the lethal concentration, and the average concentrations should cause no sublethal effects. Sometimes it is required that full-strength effluent should not be lethal to any of the species tested. Those toxicity requirements are at least as stringent as Canadian and Ontario ones.

West German regulations are not overly strict at present for the allowable maximum discharges of conventional pollutants. However, stricter controls are proposed for early 1989, including a maximum discharge of organochlorines of 1.0 kg of organic halogen [9] per tonne of bleached pulp. Furthermore, there is already a fee structure based on the discharged **amounts** of oxygen demand, solids, and toxicity

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[9] Halogens are members of a family of chemical elements including chlorine. For all practical purposes "Organic Halogen" is equivalent to "Organic Chlorine" in the kraft pulp industry, since the other halogens are essentially absent.

to fish, and it would appear that a small Canadian kraft mill might be charged about half a million dollars if those regulations prevailed here.

In Sweden, regulatory effort has shifted from controlling BOD to controlling the discharge of Total Organic Halogen (normally expressed in Sweden as "total organic chlorine", or "TOCl") by means of specific limits in kilograms of TOCl per tonne of pulp produced. It is not uncommon for Swedish regulators to specify the technology to be installed in mills, but we do not consider that to be an effective approach.

1.7 Pulp Production Processes

Kraft and mechanical pulp are the two predominant types of wood pulp produced in Ontario, as in the rest of the world. The discussions in this report are restricted to kraft pulp. In the case of the several Ontario mills which manufacture other, non-kraft, products on the same site as a kraft mill, the content of this report should generally be interpreted as referring to the kraft mill component only.

Unbleached kraft pulp is manufactured by separating wood into its individual fibres by cooking wood chips under pressure and elevated temperature in a digester with strong alkali. The lignins and other non-fibrous material are mostly recovered as black liquor and incinerated, and the losses from this process represent items of major concern in most mill effluents. Typically 96 to 99.5% of the black liquor is recovered, and the rest becomes part of the mill effluent. The efficiency and reliability of this recovery system has a major impact on all effluent parameters except those related to chlorinated organics.

The pulp is usually bleached by chlorine and related chemicals, and then dried for sale or used on site for papermaking. Traditional bleaching processes cause about 7% of the weight of the pulp to be discharged to sewer in the form of a wide variety of compounds, including organochlorines.

Prior to 1970, kraft pulp bleach plants were based entirely on the use of chlorine and chlorine compounds. However, since the early 1970's, oxygen has partially replaced chlorine in many overseas mills, as well as a few US mills and one Canadian mill. The principal reasons for substituting other chemicals for some of the chlorine used in bleaching systems are to reduce chemical costs and improve effluent quality. The substances removed from the pulp by treatment with oxygen can be recycled to the chemical recovery system, thus permitting incineration of the organics and other compounds which give rise to the organochlorines, BOD, toxicity and colour in the bleach plant effluents.

1.8 Environmental Control Technology

The general trend in the pulp industry is to use in-plant techniques such as high efficiency brownstock washing, condensate stripping, oxygen delignification, extensive recycle of process streams and spill collection to improve effluent quality and reduce or even eliminate the need for external effluent treatment systems. In general these in-plant measures are environmentally desirable, since most eliminate the formation of pollutants, and rarely have undesirable side effects. Those in-plant measures which are logical steps toward an ultimate goal of the zero-effluent mill are of course particularly desirable in the long term.

However primary treatment is usually necessary, and secondary treatment may be required to reduce the impact of the treated effluent to acceptable levels for the specific environment in which the mill is located. In many mills, external effluent treatment processes are installed to treat part or all of the effluent from the

mill. The traditional external treatment technologies are effective in reducing suspended solids and BOD discharges to very low levels, but they are of limited reliability in reducing acute toxicity to fish, and only modestly efficient in reducing discharges of organochlorines and persistent organic compounds.

In general, **external effluent treatment systems deal with persistent pollutants by concentrating them in a side stream sludge** which is a very small fraction of the effluent flow. This sludge can perhaps be incinerated or landfilled harmlessly, but is **almost always an environmental problem**. The aerated lagoon process is exceptional in this regard, since some substances are converted into harmless material, usually in the anaerobic conditions which are maintained in the benthal sludge in a well designed and operated lagoon. The most significant example relevant to this report is the ability of aerated lagoons to convert organochlorines to harmless chlorides.

Much of the current in-plant effluent control technology inherently avoids the problem of side stream disposal by eliminating generation of the pollutants. The practice of substituting chlorine dioxide for chlorine in the bleach plant is an excellent example of this approach which is being implemented increasingly around the world, especially in North America.

Other in-plant environmental control techniques modify the process so that substances traditionally discharged to the sewer are incinerated in existing process equipment such as the recovery boiler. Oxygen delignification and many spill protection systems are examples of this category.

The four major, currently proven, technologies which we consider appropriate to the current needs of Ontario mills are shown in Table 1.2.

Table 1.2 Simplified summary of effect on effluent quality of adopting some alternative technologies in existing mills.

Process Modification	Reduction in BOD	Reduction in organochlorine	Reduction in fish lethality	Comments
Oxygen delignification	20 - 40%	up to 50%	Appreciable	Retrofit feasible
Chlorine dioxide substitution	None	up to 50%	Variable results	Retrofit feasible
Extended delignification	Modest	up to 20%	Little	Retrofit difficult
Biological treatment	Up to 90%	Up to 33%	Appreciable	Retrofit feasible but requires space

Other technical solutions may exist or be developed in the future for improving kraft mill effluent quality.

Extensions of in-plant effluent control technology which will completely eliminate chlorine compounds have been researched at the laboratory level, and we consider that there is now sufficient knowledge available to build at least a small pilot plant with a view to building full scale industrial systems within a few years. We consider that such research should receive high priority.

1.9 Effluent Quality in Ontario and Elsewhere

The average suspended solids discharge from Ontario mills is about 60% of the average from Canadian mills. The average BOD of Ontario kraft mill effluents is slightly above the Canadian average, and is greater than that of all other provinces except Québec.

The average discharge of BOD per tonne of output from Ontario mills is about four times higher than the US average, while suspended solids discharges from Ontario kraft mills are comparable with those in the US. Only two Ontario mills would meet US regulations on BOD and Suspended Solids.

The average discharge of organic chlorine from the nine Ontario kraft mills is 6.5 kg/t pulp. Finnish bleached kraft mills discharge an average of approximately 5 kg of organic chlorine per tonne pulp,and Swedish mills probably average somewhat under 4 kg/t. US mills are estimated to discharge under 5 kg/tonne since all have secondary treatment and many use either high chlorine dioxide substitution or oxygen delignification.

1.10 Aquatic Toxicity Tests

A lethal test with fish or other organisms is a convenient way of exploring toxicological problems and monitoring effluents. The Canadian federal toxicity test for pulp mill effluent is a simple, single-concentration, pass/fail test as is appropriate for monitoring. It requires that not more than 20% of rainbow trout should die in 65% concentration of effluent. The Ontario definition of toxicity appears to be "not more than 50% mortality in full-strength effluent" (i.e. LC50 $\geq$ 100% effluent).

Some rapid new tests based on bacteria could be most beneficial for use in mills. They can be run almost like chemical tests with bottled reagents, and give results that are reasonably consistent with those for trout lethality. Since micro-organisms are often among the most sensitive of aquatic organisms, these should be recognized as legitimate toxicity tests.

There is scope for regulatory tests based on sublethal effects. Sublethal toxicity can now be assessed in 7 days by measuring growth of newly-hatched fathead minnows or reproduction of the water-flea *Ceriodaphnia*. Mutagenicity of an effluent can also be evaluated by a variety of rapid tests. Such laboratory findings on sublethal effect should be, and have been, validated by field surveys of effects on the aquatic communities in the receiving waters.

The regulatory test with acute lethality of fish is based on concentration of toxic material in the effluent. This discourages water conservation and more importantly is a disincentive for installing many process modifications that are environmentally desirable.

Ecologically, it is more reasonable to regulate by the **amount** of toxicity discharged rather than by concentrations in the effluent. That can be done by using a fixed maximum water allowance per tonne of pulp produced when determining the LC50. An effluent allowance of 175 m^3/tonne, using the static test of the Ministry and a criterion that LC50 must equal 100% or more, would maintain the original strictness of the federal toxicity test.

1.11 Toxicity of Kraft Mill Effluents to Aquatic Organisms

Most kraft mill effluents with only primary treatment are lethal to fish. However these wastes are only mildly toxic and would not normally cause direct mortality in the receiving water, given a location with adequate mixing and dilution. For the 6 Ontario kraft mills with only primary treatment, lethal concentrations typically ranged from 12% effluent to more than 100% (non-lethal).

Secondary (biological) waste treatment may or may not render an effluent non-lethal. Of the three Ontario kraft mills with aerated lagoons, one had achieved a consistently non-lethal effluent by 1985-86, but the other two mills had effluents that were as lethal as untreated ones. **If secondary treatment is not satisfactorily removing acute lethality, then it will not be reducing the sublethal effects either.**

Resin acids contribute a major proportion of the acute lethality of kraft mill effluents. However these substances decompose fairly readily and do not pose a major problem of persistent toxicity. Fatty acids contribute a smaller amount of toxicity, and also decompose.

The most important sources of acute toxicity in the mill are often leaks and small-volume spills of process fluids, brownstock washing filtrates, both acid and alkali bleach plant streams, and blow heat condensate. Potential remedies are improved design and operation of the processes, changing the processes used, neutralization of waste, or biological treatment. Two beneficial changes in process are substitution of chlorine dioxide for chlorine in the bleaching process, and oxygen delignification with the washer filtrates recycled to the recovery boiler. Those changes reduce or eliminate mutagens in the effluent, and they also reduce general sublethal effects on aquatic organisms as clearly shown by Swedish studies in real and artificial ecosystems.

Judging by a great deal of sublethal toxicological work, aquatic animals would be protected from overt whole-organism effects if the average concentration of kraft mill effluent in a waterbody were 5% of the LC50 for that effluent, and the maximum concentration were 10% of the LC50. For example, if the LC50 were 30% effluent, the allowable average after dilution would be 1.5%. Some Swedish studies suggest considerably lower effect-concentrations, but we are uncertain of the relevance to Ontario waters.

Kraft mill effluent can cause off-flavours in fish at concentrations in the vicinity of 1%, similar to concentrations causing sublethal physiological effects in the fish. Within the mill, digester and evaporator condensates are important sources of tainting chemicals, but the bleach plant is not. Secondary waste treatment reduces tainting by a factor of about 10, for either fish or drinking water, and aeration also decreases fish tainting.

Most of the mutagenic chemicals in kraft mill effluent are in the chlorination effluent of the bleach plant. Some of them have been identified as various chlorinated low-molecular-weight organic substances. These mutagens do not appear to be strongly persistent in the environment.

Low dissolved oxygen interacts with the toxicity of kraft mill effluent, and these things increase each other's effect. It is important to maintain reasonable concentrations of dissolved oxygen in the receiving water, not only because of the deleterious effects of low oxygen, but also because of this interaction with toxicity.

1.12 Organochlorine Substances

A variety of chlorinated organic chemicals are produced by bleaching in kraft mills. The average Ontario bleached kraft mill produces about 33 tonnes of chlorinated organic substances per day. About 300 low-molecular-weight organochlorines have been identified in bleach plant waste, but those represent less than 10% of the total weight of organochlorines.

Chlorinated phenolics and chlorinated resin and fatty acids account for much of the acute lethality of bleach plant effluent. Most of them are lethal to fish at about 1 mg/L or a few mg/L. These low-molecular-weight substances are moderately bioaccumulative in fish, but are readily excreted if the organism moves to clean water. The chemicals are only moderately persistent in the environment, but are only partially removed by secondary waste treatment. High-molecular-weight chlorinated lignins are not very toxic to fish, but slowly degrade to toxic low-molecular-weight forms.

The real cause for concern is not the common chlorinated phenolics and resin acids which cause acute lethality and have received the most study. The worry is the unknown degree to which highly toxic and persistent substances are formed and escape to the environment. Very small amounts of chlorinated dioxins are formed, and it can be safely assumed that there are other undiscovered highly toxic substances.

Swedish industry and government have carried out research programs on environmental aspects of bleached pulp waste for a decade, in the laboratory and in the Baltic Sea. Some effects on fish, such as erosion of fins and failure or delay of gonad development, were related to bleach plant waste, since they were not found near an unbleached kraft mill. The Swedish research provides some evidence that organochlorines formed in bleached kraft mills are dangerous. Their emphasis on reducing organochlorine discharges seems to be also derived from a rationale that chlorinated organic substances in general have proven deleterious in past experience.

We tend to agree with that point of view inasmuch as some of the worst bioaccumulative toxic substances over the past few decades have been chlorinated organics. DDT and PCB accumulated in food chains with loss of reproductive capacity in fish, birds and some other animals. They spread themselves through ecosystems before scientists were aware that there was a problem. We are concerned to hear of recent similar situations, with reports of reproductive failure in lake trout from Lake Michigan, and the associated documentation of 476 persistent organic chemicals in the bodies of Great Lakes fish.

The recent furor over dioxins confirms that the public is concerned about the discovery of small amounts of dangerous substances in wastes from bleached kraft mills. Dioxins have been found in almost all bleached kraft mill effluents analysed by laboratories with extensive experience in dioxins and similar substances. There does not seem any reason to wait for the discovery of other subtle toxicants in bleach plant waste. There are known methods for reducing organochlorine discharges, some of them economically advantageous, and others that are at least without severe economic penalty. It seems evident to us that Ontario mills should start now to significantly reduce their output of organochlorines.

Concern about organochlorines is evident in some customers of the products from the Ontario pulp industry, and Europeans have indicated their intention to restrict imports of pulp and paper products which contain organochlorines.

1.13 Determination of Organochlorine in Effluent

There is considerable debate on whether TOCl, AOX, APHA TOX, or one of the other recently developed techniques is the most appropriate for analytical determination of the discharge of organically bound chlorine. There are sufficient differences between the chemistry of the various analytical procedures for determination of total organically bound chlorine that exact conversion factors between them cannot be developed.

Experience in determining organochlorine content of effluents is relatively recent, and the most widely used method to date, ("Swedish TOCl") is in the process of being abandoned by its originators. After reviewing various procedures, and interviewing analytical chemists with combined first hand experience in all these methods, we consider that the Total Organic Halogen (TOX) method of the American Public Health Association is the most appropriate for Ontario. It is the most widely used in the US, is a practical and well established procedure, and should produce results similar to the AOX method which will probably be used in Europe.

A useful mathematical technique was described by Germgård (1983), and is based on the input quantities of chlorine and chlorine compounds used in bleaching the pulp. A mathematical approach would allow the Ministry to specify objectives clearly, and industry to engineer and install systems to reduce the discharge of organochlorines with an assurance that the operation would be successful, despite the relatively immature stage of development of the analytical procedures and the ability to predict the exact degree of reduction.

When comparing technical literature, regulations, or other data on organochlorines, it is particularly important to consider the analytical or calculation procedure used, since the rapidly developing knowledge and high levels of media attention have led to considerable confusion.

1.14 Chlorinated Dioxins

The "dioxin" of the news media can be translated as 210 chemicals belonging to two families, the chlorinated dibenzo-p-dioxins and the chlorinated dibenzofurans. Two important members from a toxicological viewpoint are 2,3,7,8-tetrachloro-p-dibenzodioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF).

Toxicity of these chemicals is measured in parts per trillion (ppt). The most toxic is 2378-TCDD, and other isomers may be expressed as approximate **"Toxicity EQuivalents"** or TEQs of that substance, by applying appropriate factors.

The main sources of chlorinated dioxins and furans are various unintended by-products of manufacturing processes , or burning of wastes. Increased amounts have been in the environment for 3 or 4 decades but are better documented in the last few years because of improved analytical procedures.

In kraft pulp mills, the bleach plant contributes almost all of the chlorinated dioxins and furans as an infinitesimally small part of the total organochlorine emissions. The major destination of the dioxins can be the liquid effluent, the sludge from waste treatment, or the bleached pulp, but any of the three outputs can be important, depending on the mill.

We assume that reduction in chlorine use in a mill would reduce the production of chlorinated dioxins and furans, and some recent studies support that theory.

The total contribution from pulp mills to the Ontario environment appears to be minor, of the order of one four-hundredth of that from other sources. An average bleached kraft mill might produce 11 mg per day of 2378-TCDD (TEQ) in the liquid effluent, much less than the average of 520 mg/d TEQ released to the air from a municipal garbage incinerator in Ontario. Sludge from municipal waste treatment plants may be higher in these contaminants than sludge from bleached kraft mills. Direct intake by humans from paper products would appear to be trivial.

Chlorinated dioxins and furans are almost insoluble in water, so they tend to travel through ecosystems on particles or as residues in living organisms. Therefore the discharges from pulp mills and subsequent accumulation in fish gain importance as a potential source of contamination. Larger fish from some polluted locations may contain 20 parts per trillion, or more. The chlorinated compounds accumulate to higher concentrations in predators such as fish-eating birds. For humans, intake from contaminated fish could be the most important source for the very few locations in Ontario, where frequent fish-eaters could exceed the recommended Acceptable Daily Intake (ADI). Still the risk should be kept in perspective, since the ADI, continued for life, may be equivalent to one chest x-ray.

We fear that media publicity about kraft mills as a source of chlorinated dioxins may divert energies from productive avenues of pollution control into blind alleys of ill-conceived, routine, and expensive surveys of "dioxin" concentrations.

Chlorinated dioxins and furans may not be as toxic to humans as is commonly believed. They do not seem to be genotoxic (mutagenic) so they are not considered to be a standard "initiator" of cancer, although they may promote cancer. There have been numerous human exposures through accidents and industrial use, but the only effect clearly and consistently demonstrated in follow-up studies has been severe skin eruptions ("chloracne"). The studies have not shown increased incidence of cancer or earlier mortality, and there is not enough evidence of chronic effects in humans to estimate allowable exposures directly. Experiments with mice and rats indicate a no-effect level of 1 nanogram per kilogram of body weight per day (ng/kg.d) for various sublethal effects. The ADI for humans has been derived from the animal experiments by applying a safety factor of 100, thus estimating an ADI of 0.7 ng 2378-TCDD/day for a 70-kg human. That ADI may be quite conservative.

1.15 Chloroform

Appreciable amounts of chloroform are formed in some bleached kraft mills, particularly in hypochlorite bleaching stages, where the latter are used. Because it is a known carcinogen and is volatile, there has been concern about concentrations in the workplace and near waste treatment lagoons. It does not seem to be a major problem for aquatic organisms.

The US EPA is actively studying the chloroform question and regulations are expected to be forthcoming during 1988. The measures to reduce organochlorines recommended in this report will tend to discourage the use of hypochlorite bleaching, and to that extent the problem will be reduced, without any action by MOE specific to chloroform.

1.16 Economic Implications

The economic implications of requiring pulp producers to comply with regulations or Control Orders based on the recommendations in this report are dependent on which level or levels of achievement are selected by the government, and vary widely from mill to mill. Not surprisingly, those mills which have already invested extensively in water pollution control systems would incur lower future expenditures than those which have not.

Capital and operating costs for achieving each level of environmental protection defined in Table 1.1 were calculated, but the costs for specific mills are not presented here since they are based on our detailed knowledge of operating data for mills that must compete.

Capital costs of achieving each level vary widely from mill to mill, and depend on local conditions, the extent to which each company has already invested in environmental protection, and the size of the mill. The average capital cost of achieving level II effluent quality would be approximately $50/tonne of daily pulp capacity, while the investment required to attain level III would require approximately $20/t more. The average capital investment cost of achieving level IV if required immediately by the Ministry would be substantially greater at $130/daily tonne. The highest capital cost we estimated was $191/daily tonne.

The changes in variable operating costs are shown in Table 1.3. Most mills would experience a reduction in variable operating costs. This is primarily due to reductions in the cost of bleach chemicals by replacement of most of the chlorine with oxygen and chlorine dioxide. **Note that the mills which would incur the greatest operating savings would generally also incur higher than average capital costs, but not necessarily the highest costs mentioned above.**

Table 1.3 Changes in variable operating costs of achieving each level of environmental protection. Dollars per tonne kraft pulp.

Level	Lowest [10]	Highest
II	- $11.2	+ $2.4
III	- $11.2	+ $1.9
IV	- $14.0	+ $2.4

Generally, the smaller mills would incur substantially higher capital costs per tonne of pulp produced than the larger ones. In most cases the costs of reducing BOD, if required, are greater than the cost of complying with the recommended limits on organochlorine.

10 *Negative numbers represent a saving in variable costs compared with current operations.*

2. INTRODUCTION

2.1 Raison d'être

The pulp and paper industry in Ontario is a significant consumer of water. Existing processes for the manufacture of pulp lead to the discharge of large volumes of effluent into receiving bodies. In 1986, the 9 mills in Ontario producing kraft pulp discharged an estimated 891,000 cubic metres of effluent per day. This is equivalent to the water used by a city of 2 million people.

The Ontario Ministry of the Environment, under the authority of the Environmental Protection Act and the Ontario Water Resources Act, has the responsibility for regulating the quality of effluent flowing into surface waters. The Ministry exercises control over effluent quality by the issuance of regulations and Control Orders (regulatory instruments authorised under the Environmental Protection Act for individual dischargers).

In principle, the existing regulatory framework relies heavily on three main parameters of quality for mill effluent: a standard acute lethality test on fish (the so called acute toxicity test); limitations on the discharge of biochemical oxygen demand (BOD); and limitations on the discharge of total suspended solids (TSS).

In contrast to the situation in the United States where the US Environmental Protection Agency (EPA) specifies effluent quality parameters which are essentially identical across all point-source discharges in a given sector of the pulp and paper industry, the approach in Ontario has been to negotiate effluent quality parameters on a mill-by-mill basis. The requirements written in the Control Orders in Ontario are effectively determined by a (typically) lengthy negotiating process between the mill and the Ministry. One result of this highly individualised process for determining Control Orders is that effluent quality requirements and standards vary widely across mills in the province. Some Control Orders specify that the effluent must pass the acute lethality test on fish and meet negotiated limits on BOD and TSS. Not all control orders, however require mill effluent to pass the acute lethality test. In addition, some Control Orders do not place limits on BOD or TSS discharges.

There has been considerable debate over whether or not the existing regulatory framework, in terms of both substance and process, adequately addresses the problem of defining and securing an acceptable level of effluent quality for pulp mill discharges.

In particular, it has been implicitly assumed that a mill effluent which passes the acute lethality test on fish poses little threat to the aquatic environment or, by implication, to humans. Environmental groups have noted that only 3 of the 9 kraft mills in the province can meet the acute lethality test (only two of the 8 mills producing bleached pulp by the sulphate process have effluents that are, sometimes or always, capable of passing the test). In addition, that progress in reducing water pollution from pulp mills in Ontario has been slower than in some other major producing regions. Industry members have been critical of the acute lethality test as being a biased indicator of water quality and have been reluctant to invest money in processes that would allow effluent to meet the standards set by the test. Industry is also aware that the MISA programme (Municipal/Industrial Strategy for Abatement), announced by the Province in June 1986 may well require mill effluent to pass a more detailed set of requirements than those outlined in existing control orders. Whereas the existing effluent quality requirements are mainly limited to acute toxicity, TSS and BOD, the MISA framework is expected to be far more detailed in terms of specifying permissible levels for the discharge of given chemical substances. In particular, the MISA program focuses on persistent

toxicants, and may control the discharge of effluents that contain chemicals which are toxic only sublethally or with chronic exposure, and are non-lethal in short exposures.

In the last few years there has been growing concern, both in Canada and abroad, with the environmental fate of constituents of the effluent from mills producing bleached kraft pulp. This concern has focussed attention on the chlorinated organics that are produced in the traditional bleaching process and are subsequently discharged to the environment.

Our committee has been charged by the Ministry of the Environment with examining in detail the following general issues:

> identify methods of reducing the discharge of acute and persistent toxic substances from kraft pulp mills;
>
> examine current Ministry of the Environment static toxicity testing procedures and recommend possible improvements or alternatives;
>
> attempt to identify the components of kraft mill effluent that cause toxicity; and
>
> examine the economic implications of installing and operating toxicity reduction measures.

2.2 Approaches Taken

We could not, during this study, initiate original scientific research on the relationship between the constituents of pulp mill effluent and their environmental fate and effects. Research of that nature typically takes an extended period of time and is also very expensive. Fortunately there is a large and growing body of scientific literature which addresses many of the technical relationships that are central to an understanding of the problems surrounding effluent from the kraft pulping process, both in terms of how toxic substances are produced and the effect of such substances on the environment.

We have examined detailed technical information from a wide variety of sources. Our analyses and subsequent recommendations have been based on an extensive review of the literature together with visits to kraft pulp mills. In addition, we have consulted freely with experts in industry, government and academia, in Canada, the United States and Scandinavia, on various issues germane to this study.

Our recommendations are firmly based on what can best be described as existing proven technology; that is, production processes which are operating successfully in more than a single mill. We are very aware that the elimination of toxic substances in the effluent from kraft pulp mills cannot be accomplished instantaneously. Large reductions in the flow of toxic substances will require the adoption of short, medium and long-run regulatory goals that are mutually consistent. Policy makers must be aware that the industry will require some lead-time in meeting new environmental standards. Industry must also recognise that protection of the environment needs to be accorded a higher priority than has occurred in the past and that in consequence technical and financial resources must be committed in order to attain environmental goals economically and effectively.

The committee's first responsibility is to recommend ways of reducing the discharge of toxic substances from kraft pulp mills (see terms of reference above). Almost all such toxic discharge is with the liquid effluent and therefore we have taken "toxicity" to refer primarily to effects on aquatic ecosystems. The

assumption is that satisfactory protection of those ecosystems will also protect humans, and in that sense the aquatic organisms function as early warning systems of any toxic dangers. Items of particular importance to humans have been considered, however, such as drinking water, tainting and toxic contamination of fish.

Toxicity can be measured only by its effect on living things. For almost two decades, the toxicity of effluents from Canadian pulp mills has been measured by a standard test of short-term lethal action on rainbow trout. That test was promulgated in Canadian federal regulations in 1971, and Ontario has adopted very similar requirements for a rainbow trout test. We agree with statements by MOE, and concerns expressed by public environmental groups, that there should be no slackening of that toxicity standard. Accordingly, part of our basic approach has been that the trout test should continue as a primary standard, to satisfy the same requirements for amounts of toxic material discharged, as prevailed when the test was designed in the early 1970s.

At the same time, we applaud the initiatives in the MISA program (although not necessarily all of the methods), because we agree that the really dangerous toxicants are the persistent ones. Another part of our basic approach was therefore to emphasise control of any such persistent or bioaccumulative toxicants that might exist in kraft mill effluent. It may not be generally understood that these subtle toxicants are not necessarily detected by the rainbow trout test. Therefore we set out to recommend approaches that would measure and control any persistent toxicants.

Our approach also fits the general MISA philosophy in other ways. As stated, we have based our recommendations on existing proven technology, and MISA has its approach of "Best Available Technology", which includes changes in manufacturing processes, substitution of chemicals and in-plant control as well as the waste treatment that is often thought of first. We have suggested criteria to protect the aquatic organisms in the receiving water, and MISA has its "water quality track" with the same objective of protecting individual bodies of water.

2.3 Economic Importance of the Pulp Industry to Ontario

Pulp and paper mills make up the leading three-digit manufacturing sector of the Canadian economy in terms of value added. Based on data for 1984, pulp and paper mills accounted for 6.6% of value added in Canadian manufacturing. (Statistics Canada (31-203) 1984) [1]. The pulp and paper mill sector is the third leading sector in terms of providing manufacturing employment. In 1984, the sector provided just under 5% of the country's manufacturing jobs. At the four digit level of disaggregation, the newsprint sector is more important than the pulp mill sector in the Canadian economy. Newsprint mills rank second in terms of value added (behind the motor vehicle industry) whereas pulp mills rank ninth.

The pulp and paper industry is slightly less important in the Ontario economy than it is in the national economy. In 1984, the industry accounted for 3.2% of value added in manufacturing in the province and 2.5% of production workers employed in manufacturing sectors. The pulp and paper industry ranked fifth in value added behind motor vehicle parts, motor vehicle manufacturers, primary iron and steel and other machinery and equipment. As is the case in the national economy, the newsprint industry is more important in terms of both value added and employment than is the pulp mill sector. (It should be noted

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1 The Paper and Allied Product Industries (Code 27) is referred to as "two-digit" industry. The industry includes four separable "three-digit" sectors (Pulp and Paper, Asphalt roofing, Paper box and bag and other converted paper product industries) The three-digit pulp and paper digit sector contains a number of "four-digit" industries. Pulp, newsprint, building board and other paper industries.

that in both the Canadian and Ontario economies the importance of the pulp and paper industry measured by value added will probably be greater for 1986 and 1987 than for 1984. Market prices for both pulp and newsprint, but especially for pulp, have increased in real terms since 1984 and in addition operating rates and shipments have increased over those recorded in 1984.)

The pulp and paper industry is of crucial importance to the economy of Northern Ontario (Anderson and Bonsor 1985). Communities such as Espanola, Dryden, Fort Frances, Marathon Red Rock and Terrace Bay are almost completely dependent on the industry as a base for local economic activity. In Thunder Bay, the industry is the major component of the economy's export base. Large reductions in employment in the industry in these communities would clearly create a significant problem for local employment levels.

2.4 Recent Relevant Studies

Each member of the committee used an individual collection of technical literature and information in preparing this report. Each member also conducted a search of new and relevant literature in his particular field. For searching and collecting, there was heavy use of the bibliographic database of the Institute of Paper Chemistry (Appleton, Wisconsin) and the library of the Pulp and Paper Research Institute of Canada (Paprican, Montreal). Certain recent reviews of the scientific and technical literature were also most useful, but we always formed our own interpretations by cross-checking and by consulting original publications for important items. For example, we checked through somewhat more than 500 original papers and reports on toxicology and water pollution.

Some very up-to-date and excellent toxicological reviews were of great assistance. To some extent, therefore, it has been possible to draw conclusions and make recommendations without burdening the reader with a lengthy repetition of all the supporting findings by individual workers. Readers are frequently referred to sections of those other reviews for further detail. In particular, the review by McLeay (1987) on "Aquatic toxicity of pulp and paper mill effluent", partially sponsored by MOE, is a magnificent source of information, and has already gained a world-wide reputation. Similarly the somewhat shorter review by Kovacs (1986) deals specifically with bleached kraft effluent, and the treatise by Brouzes (1976) remains a useful source of perspective and technical detail.

Part-way through our work, there arose considerable media and public concern about "dioxin" in pulp mill effluents and products. As a scientific issue, this can only be traced back for 3 or 4 years. A document produced by MOE (1985) was a most useful review for orientation and technical details, as was a similarly thick document from the paper industry (NCASI 1987a).

Recent Scandinavian research on pulp mill effluents, their effects, and control methods, has resulted in considerable re-orientation of ideas for most people involved in the industry, including us. We have gained much information from Swedish projects (IPK 1982, SSVL 1985, and proceedings of the International Conference on Forest Industry Wastewaters, Tampere, Finland, June 1987). Visits to Scandinavia and personal contacts there, in the USA., and of course in Canada, have also been most productive. One or more of the committee members has visited each of the 9 Ontario kraft mills during the tenure of the study.

ACKNOWLEDGEMENTS

We sincerely thank more than one hundred people who have contributed to this marathon effort.

They gave their time, advice, and information and some of their assistance was crucial in our attempt to write a balanced report.

We have not named the people, but each of them knows how much his/her contribution is valued. The report would have been be very much poorer without their help

3. PULP PRODUCTION and IN-PLANT EFFLUENT CONTROL

SUMMARY Kraft and mechanical pulp are the two predominant types of wood pulp produced in Ontario, and in the rest of the world. Unbleached kraft pulp is manufactured by separating the wood into its individual fibres by cooking wood chips under pressure and elevated temperature in a digester with strong alkali. The lignins and other non-fibrous material are mostly recovered and incinerated, and the losses from this process represent a major portion of most mill effluents. The pulp is usually bleached by chlorine and related chemicals, and then dried for sale or used on site for papermaking. Traditional bleaching processes cause about 7% of the weight of the pulp to be discharged to sewer in the form of a vast variety of compounds, including organochlorines.

This section describes the pulp manufacturing process with emphasis on the environmental aspects, including in-plant environmental protection measures. It is intended to assist readers who are not familiar with pulp mills, so contains some elementary information as well as discussion on recent developments. An overall mill process flowsheet is presented in Figure 3.2.

3.1 Wood Preparation

SUMMARY Wood must be debarked and cut into chips prior to manufacturing kraft pulp. The bark removed is normally burned, and occasionally landfilled, but wet debarking processes are a significant source of effluent toxicity, BOD and suspended solids. There is a steady trend towards mills using chips purchased from sawmills, which reduces the volume and toxicity of woodyard and woodroom effluents.

3.1.1 Woodyard and Wood Handling

On arrival at the mill, the wood is stored, for a few days to several months, prior to use in the mill. There is a substantial quantity of solid waste attached to the logs which arrive in mill yards by truck and several hundred tons of soil, bark and broken wood have to be disposed of annually in these mills. This is normally dumped to landfill and, provided reasonable measures are taken, is not a significant environmental problem.

Some mills use flumes for collection of wood from storage and conveying it to the woodroom for debarking. They require a large circulating flow of water, which becomes contaminated by bark fines, organic leachate from the bark, sand and grit. A degritter to remove heavy grit and a screen to remove the larger bark particles from the water are essential parts of any modern flume system. In some cases the excess flume water is discharged to the mill sewer, but in most cases the flume water system is integrated with the debarking system, and effluent disposal is combined with the latter. Some resin acids and other material toxic to fish can pass into solution in the water.

3.1.2 Debarking

The bark must be removed from the logs to ensure that the pulp is free of bark and dirt. The following procedures are in common use in Canada:

a) wet drums;
b) dry drum;
c) hydraulic jet; and
d) mechanical.

Only the first two systems are used in Ontario mills. Bark is removed from the logs by the friction created from the rotating drum action as the logs rub against each other. In wet drum barkers, substantial quantities of water are added at the feed end to help loosen the bark and flush the loose particles out of the drum.

Bark from a wet system is generally collected in a water flume, or conveyors, passed through a dewatering system, and then, landfilled or passed through a bark press to the bark burning furnace. Due to the mechanical action in the drums, significant quantities of material toxic to fish pass into solution or suspension in the water.

In dry drum barkers, the entire length of the drum has slots for bark removal. The drums are longer and rotate much faster than wet drum-barkers. The bark from dry drum barkers can be fired directly into bark burning furnaces. Drum barkers create waste of up to about 5% of the wood input.

Wet wood handling and barking produce cleaner logs than dry barking, due to the washing action of the water which removes sand, grit, and bark fines, but the effluent is toxic to fish due to the resin acids and other materials extracted from the bark. The wet process has traditionally been preferred by mills. However the cost of treating the woodroom effluent is high (typically a few million dollars capital) and almost all newer mills have chosen dry woodrooms and have installed efficient chip washing and pulp cleaning systems in the pulp mill to remove the dirt from the pulp.

Most bleached kraft mills specify that the bark content of their furnish should not exceed 1%. Some operate successfully with several percent bark in the wood feed, but this leads to higher consumption of cooking chemicals. Where the mill production is not limited by the capacity of the chemical recovery system, this may be acceptable. However, in recovery limited mills, the additional load on the recovery system can lead to production losses or increased BOD discharges, thus destroying the environmental advantages of dry barking.

Traditionally, many mills debarked most of the wood in summer to minimise the difficulty of handling frozen wood and to co-ordinate with river driving systems. In winter most mills heat logs before debarking, whether they are using the dry or the wet process, to thaw attached ice and snow. Most use a warm effluent such as bleach plant caustic extract, newsprint machine white water or equipment cooling water. The effluent from thawing operations contains suspended solids, has some BOD, and is slightly toxic.

Table 3.1 Comparison of effluents from barking processes (extracted from Beak 1978)

Parameter	Units	Wet Drum	Dry	Mech Chip Ring	PAPRIFER Debarking
Effluent Flow	m^3/t	3-20	0-5	0-2	0
Suspended Solids	kg/t	15-50	0-10	0-3	0
BOD	kg/t	5-10	0-3	0-1	0
Toxicity	LC50	<10%	?	?	0
Energy Consumption	kWh/t	20	21	3	60
Dryness of Bark (3)	%OD	40-55	50-55	50-55	40-55
Residual bark					
Softwood summer	%wt	.5-1	.5-1	.2-.5	2
Hardwood summer	%wt	.5-1	1-2	-	5
Softwood winter	%wt	.5-1	1-2	.5	2
Hardwood winter	%wt	.5-1	1-4	-	5

Note:

1. Above data are typical for full scale installations.
2. Effluent data exclude BOD and Suspended Solids from other sources (eg. organics introduced by use of bleach plant filtrate in woodroom).
3. Upper limits are due to use of flume to handle logs. Most systems approach lower limit.
4. No data available; toxicity is normally insignificant.

The quantity of suspended solids contained in the untreated woodroom effluent depends on the wood species, the extent of internal recycle and whether the wood has been land driven or water driven, since the latter can remove up to 50% of the bark.

The BOD and toxicity of debarking effluents varies widely, and there is little correlation between these effluent parameters and species or operating conditions, except that the less time the bark spends in contact with the water in the system, the less contaminated the effluents are. The difference between the dry and wet operations in this respects is apparent in the data in Table 3.1, where the "dry" processes would use the water primarily for log washing showers.

Typically, converting a wet process woodroom to dry barking reduces the suspended solids content of the untreated effluent from 10-50 kg/t wood to a few kg/t, and reduces the BOD by about 8 kg/t. The toxicity of the effluent from a woodroom using the dry process is typically less than 20% of that from a wet woodroom for equal effluent flow. However, the total flow from dry woodrooms is generally lower so that the current toxicity test masks this effect.

In those cases where the logs are neither thawed nor washed, the effluent from a dry barking system can be zero, but in the Ontario climate, this implies a summer only operation and/or a relatively high bark tolerance level, such as in a linerboard or NSSC mill, rather than a bleached kraft mill.

3.1.3 Chipping

For the kraft pulping process, the log is reduced to wood chip fragments generally 12 to 18 mm in length. This permits rapid penetration of the cooking liquor into the wood during pulping operations.

The elimination of fines and dust is critical in continuous pulping digesters units otherwise they tend to clog the liquor circulation screens and fill the spaces between the chips, resulting in poor liquor circulation and complete blockage of the digester. As well as disrupting production, a blocked digester upsets the process and usually causes some black liquor spills to sewer. The acceptable size chips are separated from the sawdust and slivers by passing them over mechanical screens.

Undersized chips may be passed on to the pulp mill in some cases (usually when batch digesters are used) but are usually removed for use as fuel. Chipping does not generate any significant effluents.

3.2 Pulping

SUMMARY The kraft process, also known as the sulfate process, is the dominant chemical pulping process in Ontario. Chemical recovery and bleaching technology was developed in the 1930's and 1940's, and industrial implementation has become widespread since 1945. Production of pulp and in-plant air and water pollution abatement measures are inextricably intertwined. The overall process is described in Section 3.2.1, followed by discussion of equipment and process aspects which have a major impact on effluent quality.

3.2.1 Process Description

Kraft pulping utilises an alkaline solution referred to as white liquor, typically about 10% concentration of Na_2S and NaOH, to delignify the wood for fibre separation. The series of cycles characteristic of this process is schematically illustrated in Figure 3.1, and a typical process flowsheet is shown in Figure 3.2.

The spent cooking liquors, (known universally as black liquor), are separated from the pulp by washers following cooking in the digester, and are treated in the chemical recovery system. Refer to typical analyses in Table 3.2. The recovery system regenerates the cooking chemicals of Na_2S and NaOH while utilising the heat value of the organic residue to generate steam for the process. The chemical recovery system is described in Section 3.4.

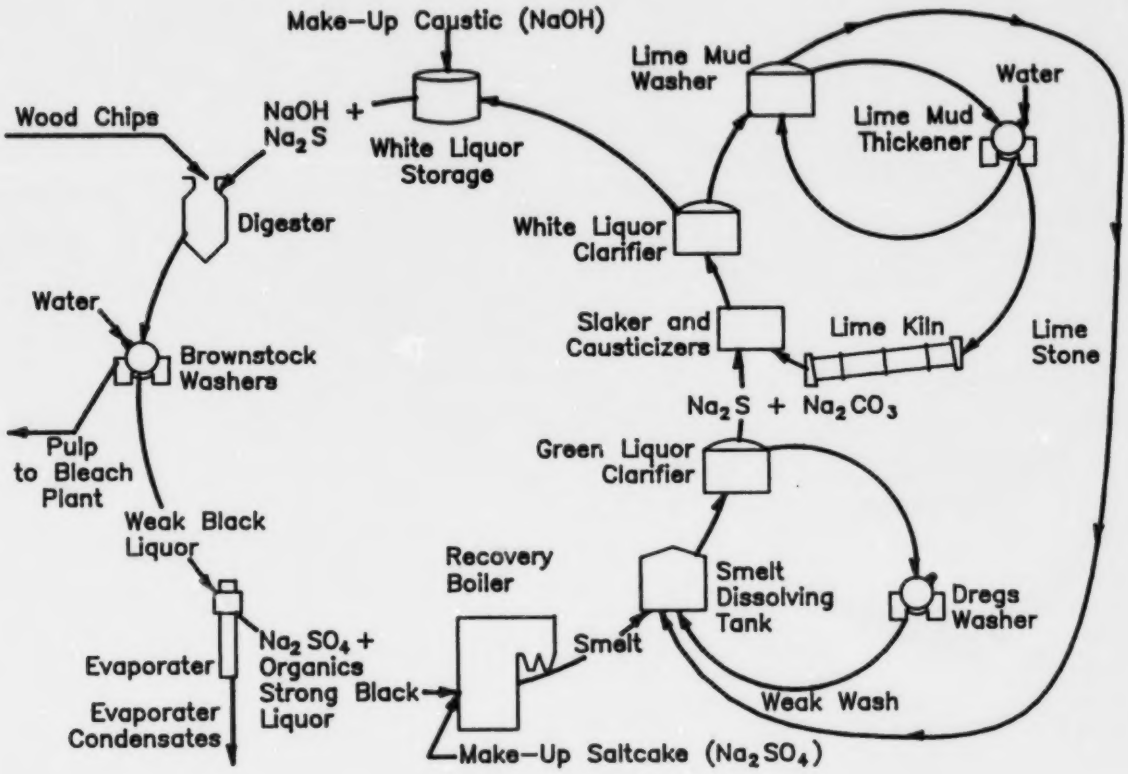

Figure 3.1 Kraft process concept

3.2.2 Digesters

The cooking process can be either batch or continuous. In the continuous cooking process, shown in Figure 3.2, the chips are pre-heated in a steaming vessel before entering the digester. Pre-steaming removes air, non-condensible gases and volatile constituents such as the terpenes. After entering the continuous digester the chips are impregnated with cooking liquor ("white liquor") at a controlled temperature to ensure uniform penetration of the cooking liquor. After impregnation, the temperature is raised to the cooking temperature of around 165°C by indirect heating of circulated cooking liquor and held there for about one hour. The pulp is then quenched to about 125°C with wash liquor.

In most continuous digesters installed after 1970, diffusion washing is then carried out in the lower region of the digester, removing a considerable proportion of the spent chemicals. The wash temperature in the lower zone of the digester is 80 - 85°C. This ensures suitable blow conditions with little or no mechanical damage to the fibres.

In batch cooking, the chips and cooking liquor are charged into the digester which is then sealed and raised to operating pressure and temperature according to a pre-determined schedule. After digestion the pulp is blown hot into a blow tank where it is diluted with black liquor and then pumped to the washing department.

Figure 3.2 Kraft Mill Process Flowsheet

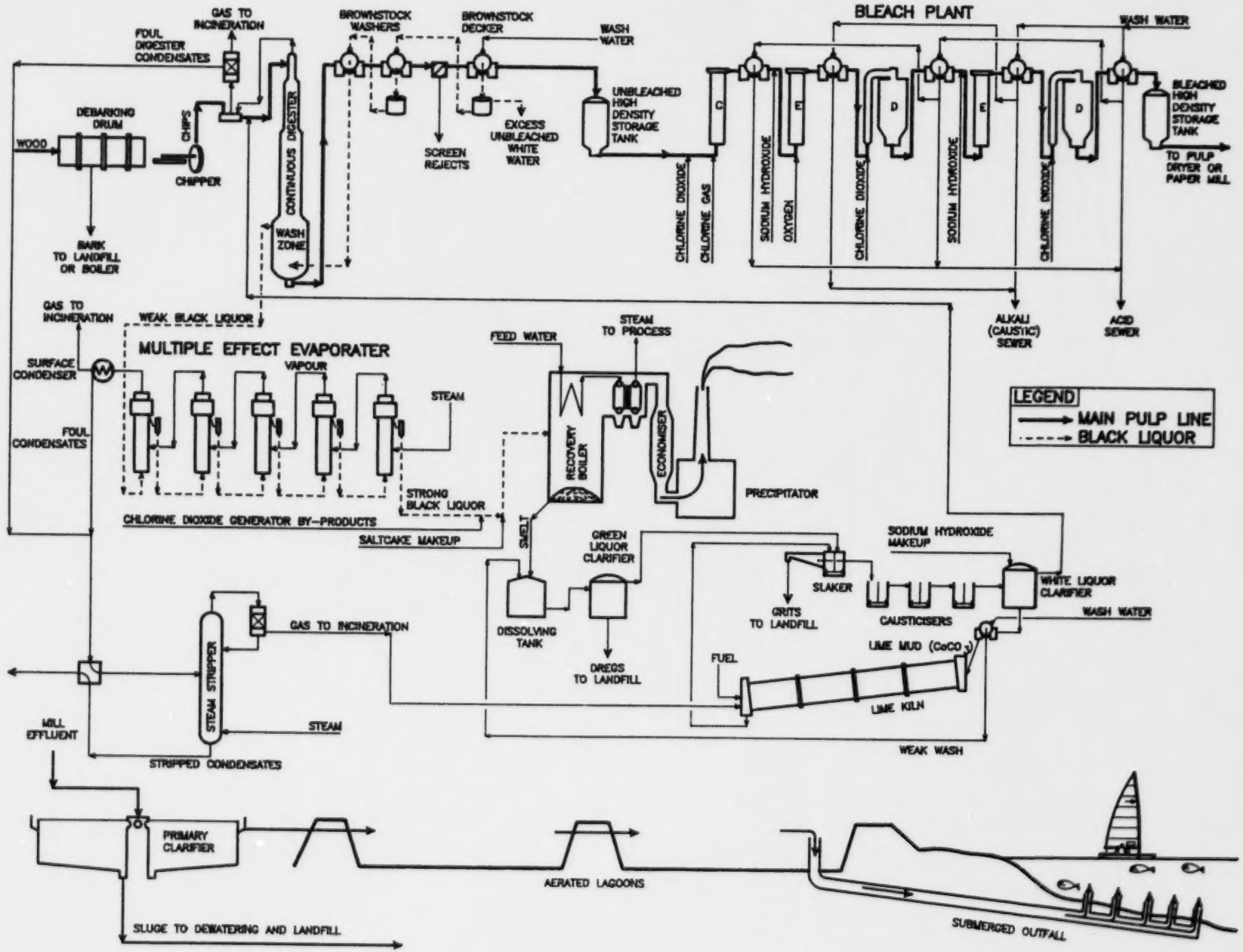

Table 3.2 Typical black liquor analysis. (percentage of dry solids) summarised from EUCEPA Symposium on Recovery of Pulping Chemicals, Helsinki, (1968).

	Pine (Mill 1)	Pine (Mill 2)	Spruce
Lignin	28.9	31.1	41
Hemicellulose and sugar	1.1	1.3	-
Extractives	6.7	5.7	4
Saccharinic acids		18.8	28
Acetic acid	3.5	5.2	5
Formic acid	4.5	3.1	3
Other organic acids	5.5		-
Methanol			1
Unknown organic compounds	19.0	5.8	
Inorganic salts	18.6	20.3	
Organically combined Na	10.1	8.7	
Unknown inorganic compounds	2.1		
Sulphur, S			3
Sodium, Na			16

3.2.3 Extended Delignification

Modified cooking, also known as "extended delignification", has been developed by several researchers.

The objective is to remove more lignin from the wood than is removed in conventional cooking, so that the amount of organic material to be removed in the subsequent bleaching process will be reduced, with consequent reductions in the required chlorine addition dose and of organochlorine discharges.

The increased delignification is achieved by introducing the white liquor progressively as the pulp is cooked, instead of adding it all at the start of the cook as in conventional cooking. Mera and Chamberlain (1987) indicated that the Kappa number could be reduced to 18 from the conventional 32 with this process, but visits to mills in Scandinavia using extended delignification have indicated more modest achievements, with Kappa numbers in the low twenties.

In theory, the organochlorine content of bleach plant effluents could be reduced almost as much by installing an extended delignification cooking system as by installing oxygen delignification as discussed in Section 3.3. However, the promising results reported by Mera have yet to be demonstrated in full scale.

Commercial systems are being marketed by Kamyr and Beloit, two well established equipment suppliers to the pulp industry. The Kamyr system, which is suitable only for continuous digesters, is marketed under the name "MCC" (Modified Continuous Cooking) and a number of systems have been installed, including at least one in Canada but none in Ontario. The Beloit system, which is suitable only for batch digesters, is marketed under the name "RDH" (Rapid Displacement Heating) and is reportedly in full scale operation in Rauma, Finland (Personal communication J.L. Chamberlain, Beloit Corp., Pittsfield, Mass).

While the installation of extended delignification in a new mill does not present any technical difficulties, there are two serious potential problems in attempting to add extended delignification to an existing mill. The first is that the load on the recovery boiler would be increased, although there are a number of possible solutions discussed in Section 3.5. The second difficulty is that for batch digesters the equipment requires a significant amount of space, which is not available in any of the Ontario kraft mills. In the case of a continuous digester, the modifications required to the pressure vessel would be impractical. We have **not considered extended delignification as practical proven technology for the purposes of this report** because of these difficulties, and because there are no immediate prospects of a new kraft mill being constructed in Ontario.

Potentially, extended delignification can be combined with the other processes for reduction of organochlorines, and appears to be a useful technology for new or radically rebuilt kraft mills.

3.2.4 Prenox

The PRENOX process has been mentioned frequently as a potential process for reduction of organochlorine discharges from kraft mills. It was developed by Samuelson and co-workers at the Chalmers Institute of Technology in Sweden, and uses Nitrogen Dioxide treatment after conventional cooking and before oxygen delignification to permit production of market quality pulp with Kappa number as low as 8 entering the chlorination stage of the bleach plant.

Laboratory work indicates the possibility of reducing organochlorine discharges by a further 50% after implementing oxygen delignification and high chlorine dioxide substitution. However, we have not considered it a proven process, since the largest plant which has been operated to date had a capacity of 3 t/day, and did not run continuously. A major pilot installation is planned in Sweden by a consortium of pulp manufacturers, machinery suppliers and chemical suppliers. Despite the positive sales statements by the promoters, we feel that commercial application is about five years away, presuming that there are no major unforeseen difficulties uncovered in the aforementioned large scale pilot project.

We are somewhat concerned about the lack of published information on the potential environmental problems which could be generated by nitrated lignins.

3.2.5 Anthraquinone

Addition of anthraquinone to the digester offers a practical and proven means of avoiding having to reduce pulp production in a mill which has installed an oxygen delignification system and lacks spare recovery boiler capacity.

In the late 1970's, a number of publications reported that the addition of small quantities of anthraquinone would increase the rate of the classic kraft pulping reaction and increase the yield, without any degradation of pulp properties. Much of the early work was by Holton and Chapman (1977) and research by others (MacLeod 1982) and a number of full scale commercial operations have confirmed Holton's findings which are the basis for this section of the report.

Anthraquinone has been used in the textile industry for many years, and the technology for using it in kraft pulp has been well known since the 1970's. Holton (1985) reports 70 pulp mills worldwide to be using anthraquinone, but none in Canada. In late 1987, at least two Canadian mills were using anthraquinone.

Anthraquinone functions as a catalyst in the delignification reaction, and permits a combination of the following improvements to be realised:

increase pulping yield by up to 2%, with a substantial reduction in the quantity of black liquor to be burned in the recovery boiler;

reduce chemical requirements by up to ten percent;

increase pulp production; and

lower cooking temperature (hence reduced energy consumption).

Similar trade-offs exist between these variables as in traditional non-anthraquinone kraft pulping, so that mills can utilise the best combination for their needs.

Any increase in yield or reduction in chemical requirements will also reduce the load on the recovery furnace, which allows the recovery and incineration of organic material which may otherwise be discharged to the sewer. An increase in pulp production would tend to increase the effluent BOD and toxicity if the brownstock washing or recovery departments were unable to process the increased amount of black liquor solids produced.

Table 3.3 Cost of various levels of anthraquinone addition to digester. (for constant pulp production of 1100 ADt/d)

Anthraquinone charge	% on wood	0.00	0.03	0.04	0.06	0.08
Yield	%	48.00	48.56	48.75	49.13	49.50
Wood input	ODt/day	2,083	2,059	2,051	2,036	2,020
Effective alkali charge	% on wood	14.50	14.13	14.00	13.75	13.50
Unit price of anthraquinone	$/kg	10.13	10.13	10.13	10.13	10.13
Cost of wood at mill	$/ODt	75	75	75	75	75
Anthraquinone charge	kg/day	0	618	820	1,221	1,616
Cost of anthraquinone charged	$/day	0	6,259	8,313	12,374	16,374
Saving on wood	$/day	0	1,802	2,404	3,578	4,735
Saving in evaporator steam	$/day	0	115	154	229	303
Savings in lime kiln fuel	$/day	0	371	493	734	972
Net cost of anthraquinone	$/day	0	3,971	5,262	7,833	10,365
Net additional cost ($ per tonne bleached pulp)	$/ADt	0	3.88	5.15	7.66	10.14
Boiler load reduction	%	0	2.7	3.6	5.4	7.2

One of the most interesting applications of anthraquinone with respect to the environment is to compensate for the increased loading on the recovery boiler when oxygen delignification is introduced, and the recovery boiler is already operating at its maximum capacity. Holton (1983) evaluated the economics of anthraquinone addition, and indicated that it could compensate for 8% increase in recovery boiler load. Table 3.3 was calculated from data from Holton, using his process data with 1988 chemical prices, for bleachable grade softwood pulp. It is assumed that the chemicals recovered from an oxygen

bleaching system would use the capacity made available, by being used as shower water in the brownstock washers, hence replacing the loss in stream generation entailed in the reduced boiler load.

Where anthraquinone is used, the reduction in alkali charge required in the digester is approximately equal to the increased sodium hydroxide production required from a recausticising plant if oxidised white liquor is used for the oxygen delignification reactor.

Table 3.3 shows that the cost of anthraquinone to reduce recovery boiler load by 5%, which would correspond to the installation of an oxygen delignification stage in a mill where the recovery boiler had absolutely no spare capacity, is about $7/t pulp This would represent about 80% of the reduction in bleaching cost achieved by the oxygen stage. (The calculation includes bleach chemical savings, energy costs etc associated with oxygen delignification). Thus anthraquinone offers a low capital, well proven way of avoiding the expense of a new recovery boiler when an oxygen delignification stage is installed in an existing mill. However, the operating cost of adding the anthraquinone almost eliminates the cost advantage of the oxygen delignification system.

Anthraquinone has been used widely in the textile industry as an intermediate in dyestuff manufacture for a number of years, in quantities exceeding current pulp industry uses, with no known reports of environmental problems. It's use in pulping has been approved by Health and Welfare Canada and the US EPA and FDA.

At least two Canadian mills use anthraquinone continuously, and report an increase of pulp yield of 1% to 2% at dosages of 0.035% - 0.05% on wood. This costs about $6 - $9 t/pulp at current prices.

3.2.6 Pulp Washing and Screening

SUMMARY The pulp is washed to separate the black liquor from the fibres, then the latter are processed in screens to remove partially cooked fibres, shives and other material which could not be bleached satisfactorily. The efficiency of the brownstock washing system is one of the keys to the operation of a kraft pulp mill with minimal water pollution. The current washing and screening processes have been in use for over forty years, but the equipment available has been improved substantially over the past fifteen years. Equipment in the Ontario mills ranges from the best modern systems with washer losses under 5 kg soda/tonne pulp to antiquated equipment with losses ten times higher.

The lignin and related material separated from the fibres during cooking (known as "black liquor") must be either recovered from the pulp stream by the washing system and routed to the chemical recovery department, or else they will be discharged to the sewer in the screening system or subsequent operations. The black liquor is toxic to fish and the toxic substances in it are relatively difficult to remove by biological treatment, so that high losses from the washing area tend to have a large impact on effluent quality.

A simplified process flowsheet of a modern brownstock washing and screening systems is presented in Figure 3.3. Note that most pipes and tanks contain black liquor in some form, so control and recovery of accidental spills is essential to protect effluent quality. The pulp from the digester contains in the order of one tonne black liquor solids per tonne of fibre, and is at a consistency of about 10%, so that there are 9 tonnes water per tonne pulp. The wash water enters the second (last) diffusion washer, and flows counter-current to the pulp, to the first diffusion washer and thence to the washing stage in the lower part of the digester body. In each washing stage, the wash water picks up more dissolved black liquor solids

and the pulp becomes successively cleaner. In the system described, about 98% of the black liquor formed in the digester would be separated from the pulp, but the remainder, including about 10 to 25 kg of organics per tonne pulp would carry on to the screens.

The screens and related pulp cleaning equipment can only operate at low consistency, so water has to be added to dilute the pulp to around 2% solids, that is to say about 50 tonnes water per tonne pulp. After screening, the pulp is rethickened on a decker to about 12% dry solids, so that excess unbleached white water must be disposed of to the sewer. In the past, a few mills simply added fresh water to dilute the pulp after the washer and discharged the excess to the sewer from the decker, but even the less efficient operations to-day recirculate much of this water. However, unless **all** the unbleached white water is recycled, the effect of this dilution/rethickening operation is that most of the organics which remain in the pulp after the last washing stage are sewered along with the unbleached white water. This is generally considered to be environmentally undesirable, and in the 1970's context when BOD was the principal criteria for defining effluent quality, this was probably true. To-day however, we must ask the question as to whether it is better to discharge these organics to the sewer in unchlorinated form, or to have them carry on with the pulp to the bleach plant, where they will be chlorinated and then discharged.

There has been a general trend toward increasing the efficiency of existing brownstock washer systems, by installing additional washing stages, better washing equipment, and by improving instrumentation. Most new systems are designed to operate with a loss of under 7 kg/t pulp unbound soda, expressed as sodium sulfate, and one Ontario mill reports 4 kg/t loss. Twenty years ago, a soda loss of 50 kg/t was not uncommon.

A systems approach to the design of the complete pulping, washing, screening and liquor recovery cycle is essential if the optimum design of the washing and screening area is to be attained. The necessary theoretical process knowledge was available by about 1960, but the amount of work and time lags necessary for the calculations of the many possible alternatives, limited the use of this knowledge in most new mill design projects. Since the late 1970's, cost effective and efficient computer based process simulation technology has been available, and is being used increasingly for the design of new mills and optimisation studies of existing installations.

The "**closed screen room**" concept has been discussed in the literature for many years, and is used in more than half the Ontario mills. Referring to Fig 3.3, if the wash water entering the second diffusion washer is replaced by unbleached white water from the decker, and the process is controlled so that all the dilution required for the screens is provided by recycled unbleached white water, then the screen room process will be "closed". In this case, the fresh wash water required to carry the black liquor solids back to the chemical recovery system would be added on the decker showers.

It is not difficult to design such a closed screen system on paper, and it is quite common for mill design flowsheets to show the only exits of liquid from the washing and screening process as being with the washed pulp and the weak black liquor which goes to the evaporators. However, the operation of a kraft screen room system without any excess water flowing to the sewer from the screening system is impractical unless all aspects of the design of the system and the equipment selection are appropriate.

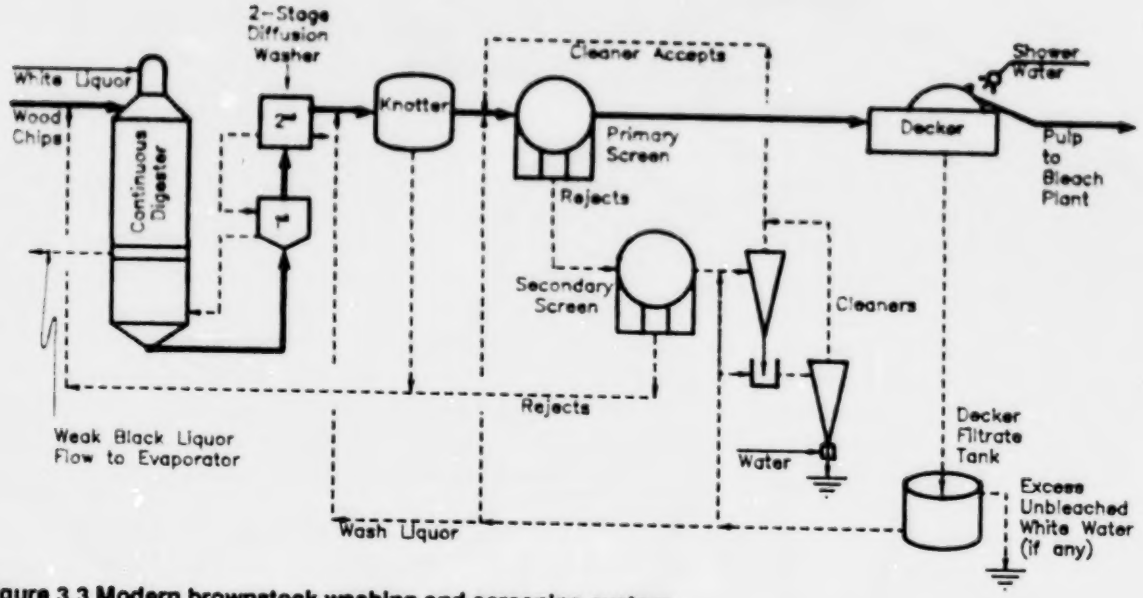

Figure 3.3 Modern brownstock washing and screening system.

The principal variables are the soda loss of the last washer upstream of the screens, the wood species and type of washing and screening equipment. The maximum acceptable unbound soda loss is, with the pulp passing from the washing to the screening department, 3 to 12 kg/t pulp depending on the wood species and equipment. The most resinous softwoods require the most efficient washing and hardwoods the least. Diffusion washers cause less air entrainment in the stock than drum type washers, so a higher soda loss can be tolerated. If modern pressure screens are used, a higher soda loss prior to screening is tolerable than where the traditional open centrifugal screens are used. In resinous type of woods, it is usually impracticable to operate a screening system without a continuous overflow to the sewer from the decker when open type screens are used.

Where the washing and screening system can be operated on a closed cycle, it results in the screen room and decker becoming an integral part of the washing system, adding an additional washing stage, which will typically reduce the effluent BOD from this area by about 60% relative to a system where there is a substantial overflow to the sewer from the decker seal tank. Most of the existing mills which have oxygen bleaching systems operate in this way, and increasing number of others do so as well.

The key difference between open and closed screening systems is that the open screen room would have a substantial overflow from the decker filtrate tank, typically 5 - 15 m^3/t pulp. Most of the residual organic material which is not recovered in the pulp washers, flows to the sewer in this stream and is one of the major sources of BOD and toxicity in the mill effluent.

It is generally desirable to operate the system so that there is no overflow of decker filtrate. However, a careful analysis of the complete black liquor system is required to determine the optimum method of operation of the available equipment. In a bleached kraft mill it may be more environmentally desirable to discharge some of the screen room decker filtrate than to have the residual black liquor reach the bleach plant, and be discharged in chlorinated form.

Foam overflows are common in some mills and contribute to effluent toxicity since the foam is rich in resin acid.Modern systems minimise foam generation by avoiding free falling liquid streams to the extent feasible and avoiding the open screens and vacuum washers which lead to air entrainment. Overflows are generally connected to other tanks as appropriate, with the ultimate overflow at a controlled point, usually the decker filtrate tank.

Improvements in closure of brownstock screening systems have taken place in several Ontario mills in recent years, and mills which consider their brownstock screening system to be closed are indicated in Table 6.2. Experience has shown that only the best systems operate on the closed process concept at all times.

3.2.7 Traditional Washing Equipment

Traditionally, kraft pulp has been washed on a series of countercurrent vacuum drum washers, as shown on the overall mill flowsheet in Figure 3.2. The pulp is alternately diluted and rethickened on drum filters, with wash water flowing countercurrent to the pulp, and being applied to a mat of pulp on the drums to displace the black liquor retained between the fibres.

This type of equipment uses large recirculating flows of black liquor and pulp, (about 100 m^3/t per stage), which can be a major source of accidental spills of fibre and organic material. Up to 99% of the washable organic material can be recovered from the pulp with this equipment, but this would normally require five stages of drum washers, whereas most mills have only three or four stages, so that only 93% - 98% of the organic material is recovered and the remainder is to sewered.

3.2.8 Diffusion Washing Equipment

Since the early 1970's, many new installations of brownstock washing equipment have used continuous diffusion washers. The earlier units operated at atmospheric pressure, while some of those installed in the 1980's operate under pressure.

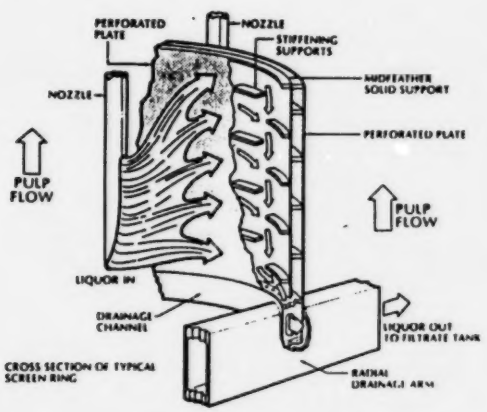

Figure 3.4 operating principle of diffusion washer.

In a typical atmospheric unit shown in Figure 3.4, pulp enters the conical bottom of the unit and passes slowly upwards through the diffuser(s). There may be one to three in series, installed vertically above one another. The washing medium is introduced into the pulp through rotating distribution nozzles, displacing the black liquor in the pulp both outwardly and inwardly to one of several screen rings, as shown schematically in figure 3.4. Displaced liquor, is collected and then pumped to the preceding washing stage. The washed pulp is discharged at the top of the diffuser tank.

A feature of diffusion washing is that the pulp remains at about 10% consistency throughout the washing process, eliminating the high flows of recycled filtrate which are required in the traditional drum washing system, decreasing pumping power and substantially reducing the volume of potential overflows.

A multi-stage diffusion washer system is also used in a few cases to wash batch digester produced pulp. Stock from the batch digester blow tank is pumped to the inlet of the diffuser tower. The pulp is thickened to approximately 8 to 9% consistency with the first diffuser. The subsequent washing stages operate as previously described.

Figure 3.3 is a simplified representation of a modern kraft pulping, washing and screening system typical of the recent installations in Canada, utilising diffusion washers and closed pressure screens and knotters. Note that even with diffusion washers the flow of decker filtrate (frequently described as unbleached white water in the literature) is large (typically 40 m^3/t) relative to the incoming shower water flow, (typically 10 m^3/t) so that any imbalance in the system is liable to cause substantial overflows to the sewers..

The **pressure diffusion washer** is an equipment variation of the traditional diffusion washers described above for single stage retrofit. The washing performance is similar to the diffusion washer, but cost in retrofit situations is usually lower and installation is simpler, so that the pressure diffusion washer has the potential to allow mills to improve washing efficiencies at lower cost that in the past. A 500 tonne/day unit would be approximately 1.5 m diameter and 11 m high, which is quite small relative to traditional designs, and lends itself to shop fabrication, which generally reduces total installed costs, and facilitates retro-fitting in an existing mill. The washing equipment is contained within a pressure vessel, which allows operation at much higher temperatures than is possible for atmospheric washers, with beneficial effects on washing efficiency. The closed design eliminates most of the risks of spills which are relatively frequent in traditional drum washing systems.

The pulp at a consistency of 10 to 12% enters the top of the pressure diffuser and moves downward as a mat between the stationary central body, and the moving perforated cylindrical screen and is removed at the bottom of the vessel. The wash medium, flows from the central body, through the pulp mat, through the moving cylindrical screen, and is extracted continuously through an extraction header.

3.3 Bleaching of Pulp

SUMMARY In Ontario kraft mills the pulp is bleached immediately after the washing/screening operation in a continuous bleach plant installed adjacent to the pulp mill. [1] *The conventional bleaching process is the source of about half the BOD, all the organochlorines, most of the colour and much of the toxicity in the effluent from a typical bleached kraft mill. In traditional bleach plants, the lignin is first converted to compounds which are soluble in alkali by treatment with chlorine, and then washed out with sodium hydroxide (caustic). The process is repeated two or three times with sodium hypochlorite and/or chlorine dioxide as the bleaching agent. There is a trend toward replacing as much as possible of the chlorine with less environmentally deleterious chemicals, including oxygen, chlorine dioxide and hydrogen peroxide, but complete replacement of chlorine is not yet technically feasible.*

The basic technology of the various bleaching processes were described by McCubbin (1983) and many other authors, and it is assumed that the reader is familiar with them.

Oxygen bleaching, or **delignification**, has been used as a partial replacement for chlorine in many mills, and it is a debatable point whether it should be considered bleaching or pulping. All variations of oxygen delignification are included in the bleaching section of this report.

Washed pulp arriving at the bleach plant generally contains about 7% by weight of lignin and related material which gives it a brown colour, similar to that of the familiar paper grocery bag. This lignin must be removed without excessive degradation of the fibres if the pulp is to be suitable for production of printing papers, whether white or lightly coloured.

To bleach kraft pulp the unwanted lignin is first converted to compounds which are soluble in alkali by treatment with chlorine, and then washed out with sodium hydroxide (caustic). The pulp is then further bleached with sodium hypochlorite or chlorine dioxide, and washed again in alkali conditions. Subsequent treatment is usually by chlorine dioxide, and where there are two dioxide stages, an intermediate alkali extraction stage with a washer is employed. The kraft mill flowsheet in Figure 3.2 includes a typical bleach plant. There are many bleaching sequences used in kraft pulp mills, and no two mills in Ontario use the same sequence, as indicated in Table 6.1.

Each washing stage generates an effluent stream, the washer filtrate, which contains the soluble matter washed out of the pulp. In the past, the filtrate from each washer flowed directly to the sewer, but to-day mills practice more or less extensive recycle of filtrates. Generally the low pH effluents from the chlorination, and chlorine dioxide stage washers are categorised as the "acid sewer", while the others are considered as the "alkali sewer" in the technical literature.

The quantities of chemicals required to bleach the pulp depend on wood species, quality of unbleached pulp, product quality targets and the bleaching equipment installed. Typically about 100 kg of chlorine/tonne pulp , in some form, is required to bleach softwoods to market quality, while hardwoods require about two thirds of this amount.

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1 The Red Rock mill is an exception in that only a small proportion of the pulp is bleached, and the remainder is used in unbleached form to manufacture linerboard.

3.3.1 Pulp Quality

SUMMARY Canadian kraft pulp is sold in the competitive international market, and is subject to the desire of papermakers and consumers of the end product, whether technically sound or not. The brightness of the finished pulp is a key criterion in its marketability, particularly in the consumer's eyes. Of all the many properties which characterise market pulp, the desired brightness has the greatest effect on effluent quality, since there are very few process alternatives for attaining the traditional 90 brightness required for market pulp, whereas there are many, less polluting, process options for slightly lower brightnesses. Unwarranted concerns about the ability of the oxygen delignification process to produce sufficiently bright and strong pulp have caused many companies to avoid using this process although it has a number of environmental advantages.

An elementary understanding of the approach used to measure **brightness** is necessary to analyse the technical literature on the environmental aspects of pulp bleaching. When a surface has the ability to fully and diffusely reflect all colours in the same proportion as they are contained in sunlight, the reflector is said to be pure white (such as a block of magnesium oxide). Absorption of one or more wavelengths will produce observable colour changes. The assessment and comparison of brightness levels requires the definition of a measuring system, a reference standard, and suitable testing equipment.

Standard Brightness in the pulp industry has been arbitrarily chosen to be the reflectance observed from a sample when illuminated with a light wavelength of 457 mu and backed by an opaque layer of its own kind. Reflection in the blue region of the spectrum (457 mu) was originally chosen for brightness because, of all the single-value measures of whiteness potential of the final product, blue reflectance is the most sensitive and relevant.

The major standards in use today are:

General Electric Brightness Metre, popular in the US;
Elrepho photoelectric reflectance photometer, popular in Canada; and
ISO standard, little used in North America, but popular in Scandinavia.

The differences in brightness values obtained by these three meters are usually only about one point on the scale 0 to 100. This apparently small difference is occasionally significant in the case of market kraft pulp mills. There are no absolute conversion factors between any two of these standards, but as a rule of thumb, 92 GE = 91 Elrepho = 90 ISO.

It is generally considered in the industry that kraft pulp must be bleached to 90 brightness to be sold readily, whereas most mills where the pulp is used on-site are satisfied with 85 brightness. Some of this difference is due to the fact that the brightness of fully bleached kraft pulp reverts by a few points in storage and shipping, and some is due to the extensive use of small differences in brightness as a sales tool, far beyond any demonstrable effect on the quality of the paper finally produced from the pulp Our lack of precision in mentioning the values "90" etc. without specifying the units is deliberate, since 90 seems to be well accepted figure regardless of the units. This apparently anomalous situation demonstrates the extent to which the desired brightness level is emotional rather then scientific. The fact that differences in brightness of one point are difficult to measure contributes to the futility of arguing whether an 89 brightness pulp is marketable or not.

Obtaining the last few points of brightness is a serious constraint on the selection of bleaching systems, and there is no doubt that it is much easier to design a bleach plant for low discharge of organochlorines and colour if the target brightness is 85 than if it is 90.

It is very difficult to put an economic value on these last few points of brightness. In principle, the marginal value of one brightness point would correspond to the amount by which a producer has to reduce the selling price of his product at 89 brightness to sell in competition with an otherwise identical pulp of 90 brightness. However there are no references in the literature to this, and none of the many industry personnel questioned could suggest a value. The most common answer was "If it is under 90 you can't sell it". This is patently un-realistic, since many mills are profitable with pulps in the 88 brightness range, while a few specialised pulps, such as those for some photographic papers, do require brightness as high as 93 Elrepho.

To summarise, brightness is a key criteria in determining the marketability of a pulp, but statements such as "We cannot use process "X" because we could not sell the product" have little credibility unless backed up with solid data.

Pulp Strength

The **strength** of the pulp is not surprisingly a key criterion of quality. There are several standard tests used, which determine the load to rupture a pulp specimen under various conditions of tension, tearing etc. Strength is a more pragmatic and less emotional criterion than brightness.

Viscosity

To control the bleaching process a property known as pulp **viscosity** is widely used. The objective is to determine the degree of polymerisation of the pulp by one of the standard tests, (e.g. TAPPI 1988). This test is useful for control of the bleaching process because it can be performed relatively rapidly and simply in the mill, and it provides a good prediction of the strength properties of the pulp whereas the above mentioned strength tests cannot be performed until some hours after the pulp has been chlorinated, and hence the results of these tests are of limited value to an operator who must adjust the chemical dosages frequently.

Unfortunately, the widespread use of viscosity determination as a process control tool has caused considerable misunderstanding of the effect of new bleaching processes on pulp quality. This is because the **relationship of pulp strength (the characteristic the customer should be concerned about) to viscosity is not absolute, but depends on the bleaching process and chemicals used**. Specifically, oxygen delignified pulp has a lower viscosity than pulp bleached entirely by traditional chlorine based sequences, whereas its strength is equal, as discussed in Section 3.3.15 below.

3.3.2 Bleaching Terminology

The following abbreviations are widely used in discussing bleaching sequences, and have been adopted in this report.[2]

C Chlorination stage, where pulp is treated with gaseous chlorine, primarily to chlorinate the residual lignin, so that it can later be solubilised.

E Caustic extraction. Dissolution of reaction products with sodium hydroxide.

Eo As "E" above, with the addition of about 5 kg/t elemental oxygen. Relatively new technology which has rapidly become popular.

O Treatment of pulp with elemental oxygen, in alkaline conditions.

Z Treatment of pulp with ozone, under acid conditions.

D Reaction with chlorine dioxide, applied as an aqueous solution.

Cd Chlorination stage with small, (<20%), sequential chlorine dioxide addition.

Dc Sequential addition of chlorine and chlorine dioxide in the same bleaching stage. Implies greater than 20% chlorine dioxide substitution.

H Reaction with sodium hypochlorite.

P Reaction with hydrogen peroxide.

Y Reaction with sodium hydrosulphite.

3.3.3 Chlorine Based Bleaching Sequences

All kraft pulp bleached in Ontario is processed by CEDED, CEHDED, CEHD, DcEHDED, or similar sequences[3]. This range of processes became established in the 1950's and has been the subject of extensive research into optimisation, the sources of environmental contaminants, and potential mitigative measures.

The efficiency of the pulp washing stages which precede the bleach plant can have as much impact on the bleach plant effluent characteristics as the bleaching process itself. Essentially, all residual lignin that is not removed from the pulp by the washing system, will be discharged with the bleach plant effluent, usually in a chlorinated form which is normally even less environmentally desirable than the lignin itself. Effective brownstock washing is therefore a prerequisite to action in the bleach plant itself to minimise effluent discharges, and any analysis of data concerning such effluents must take account of the lignin content of the unbleached pulp.

Unless otherwise noted, comments in the remainder of Section 3.3 refer to these traditional bleaching processes.

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2 Subscripts 1,2 etc. are frequently used to indicate first, second etc. (E_1, E_2).

3 The E.B. Eddy mill at Espanola is an exception to the extent that elemental oxygen is used to remove approximately half of the lignin separated from the fibres in their bleaching process, prior to chlorine based processing.

3.3.4 Effluent Flow

Although there are no regulations limiting the flow of effluent from bleach plants, it is generally environmentally desirable to minimise the flows, as a significant part of the cost of treating the effluent is directly proportional to its flow. The BOD removal efficiency of conventional effluent treatment plants is normally somewhat higher when treating the more concentrated discharge which results from low effluent flows. However, since the toxicity of a pulp mill effluent is defined by Ontario regulations in terms of the concentration of the toxic elements in it, reducing effluent flow usually increases the measured toxicity, although the mass flow of toxic chemicals to the environment may not change, and is often reduced.

All the water used in the bleaching process has to be heated to the operating temperature (30 to 75° C, depending on the stage), so that any lowering of water use normally decreases bleach plant steam consumption, and economies of a few dollars per tonne are common. Since bleach plant effluents are not normally used elsewhere in the mill, any decrease in water input to the bleaching process is normally accompanied by a corresponding decrease in effluent flow.

In the 1960's, bleach plant effluent flow was typically about 100 m^3/tonne pulp, but this has been decreased in many mills by various process modifications, which some mills discharging as little as 25 m^3/t from the bleach plant, and one notes occasional claims of effluent flows under 15 m^3/t. The reductions in effluent flows have been accomplished primarily by countercurrent washing, which is the recycle of filtrate from one washing stage to one of the preceding stages. The concept is very simple, but there are a number of constraints on the extent to which filtrate re-use can be implemented, particularly in older mills, although solutions have been developed to many of the problems.

Corrosion is the most general problem encountered, since recycle raises the temperatures in the process as well as the chloride concentrations. The pH may also be lowered, which tends to accelerate corrosion, but judicious selection of the filtrate recycle design can mitigate this to a large extent. Stainless steels with huge molybdenum content, titanium, or plastics have been used in many recently installed bleach plants for virtually all wetted parts to minimise maintenance and to allow higher chloride concentrations. Chloride concentrations up to about 6000 mg/l are considered acceptable in some mills, which theoretically corresponds to effluent flows lower than 20 m3/t, indicating that chloride concentration, in itself, is not yet an absolute limit on effluent recycle in bleach plants. Where titanium has been used for chlorination washers and other critical parts, it has been successful in reducing mill maintenance costs, and chloride concentration is eliminated as a constraint on filtrate recycle, although the capital cost is substantial.

There are a number of discussions in the literature concerning the potential of operating bleached kraft mills with little or no effluent (Environment Canada 1980), which indicate that **zero effluent will not be technically feasible in the foreseeable future, but that substantial reduction in effluent flows are attainable with known technology.**

3.3.5 Effluent BOD

The BOD of bleach plant effluent depends primarily on how much of the unbleached pulp must be extracted to attain the desired brightness. For typical softwood plants bleaching to a brightness of 90 ISO for market pulp grades, about 7% of the original pulp is extracted and discharged to the sewer. In the case of hardwood pulps, the shrinkage is normally a few percent lower.

If the pulp entering the bleach plant is not effectively washed, the residual black liquor will be removed by the bleaching equipment, substantially increasing the BOD apparently due to the bleach plant. The lignin in the residual black liquor will react with the chlorine, consuming substantial quantities of it, increasing bleaching chemical cost and increasing the concentration of organochlorines in the effluent.

Assuming that the pulp is adequately washed, there remains a range of possible trade-offs between the degree of delignification attained in cooking and that in bleaching, and mills which cook the pulp to lower Kappa numbers (signifying lower residual lignin content) will have lower bleach plant BOD discharges. However, in practice the range of possible variation in Kappa number is limited, so that bleach plant effluent BOD is normally in the range of 15 to 25 kg/t pulp, and in any one mill the decrease in bleach plant effluent BOD attainable by manipulation of the unbleached Kappa number is limited to a few kg BOD/t, except for the case where oxygen delignification is used, where BOD reductions in the order of 50% are common.

In a new mill, the potential exists to reduce bleach plant effluent BOD by a further 50% by using the "Extended Delignification" cooking techniques mentioned in Section 3.2.3.

3.3.6 Toxicity

Bleach plant effluents are toxic to fish, and in some kraft mills are the most important single source of effluent toxicity. In other mills with high losses of black liquor solids in the pulping and recovery areas, the bleach plant will be a major, but secondary, source of the total mill effluent toxicity. Since the Ontario regulation is based on concentration, there has been a tendency for the toxicity of modern bleach plant effluents to be higher than some older installations which use very large amounts of fresh water giving rise to high effluent flows.

A number of mills have modified the bleaching sequence to substitute chlorine dioxide for some of the chlorine in the chlorination stage, to decrease the effluent toxicity. The degree of substitution practiced varies from a few percent to 70%, with values around 10% being common. The latter is commonly referred to as low substitution and there can be improvements in effluent toxicity, BOD and colour when a small proportion of the chlorine is replaced by chlorine dioxide.

3.3.7 Colour

Assuming that the brown stock washing and black liquor recovery systems are operating properly, with reasonably low losses of black liquor solids, the first E (caustic extraction) stage of the bleach plant is by far the most significant source of colour in the mill effluent, as indicated in Table 3.4. The data therein are based on Rush and Shanon (1976), and are typical for the Canadian industry. The units used are APHA chloroplatinate units, so the kg/t represents an abstract quantity which is the best way of defining the total quantity of coloured material discharged.

Table 3.4 Sources of bleach plant effluent colour, kg/ADt pulp.

Stage	Softwood	Hardwood
C	50	26
E	226	78
D	11	6
E	6	4
D	1	1
TOTAL	294	115

It is clear that the E stage is the most significant source of bleach plant effluent colour, and that any in-plant modifications directed toward reducing the mill effluent colour must modify or eliminate this stream. External treatment processes for reducing effluent colour are usually based on segregation and treatment of this effluent.

A number of chlorine based bleaching sequences have been developed in research laboratories which decrease effluent colour, and to some extent toxicity and BOD, (Schleinkofer et al 1971), (Sharpe et al 1975), (Wong et al 1978), Reeve (1982), (Chan and McDonald 1983). In most cases they involve some penalty in operating cost and/or pulp quality, but they have been judged more cost effective than external colour removal systems by several US mills. They are based on the use of sodium hypochlorite to replace some or all for the sodium hydroxide in the extraction stage, and usually use a high degree of chlorine dioxide substitution in the first stage of the bleaching process.

Where an oxygen delignification step is installed upstream of the bleach plant, the quantity of lignin entering the chlorination stage is of course reduced, with corresponding reduction in colour as mentioned in Section 3.3.12. In addition, the installation of such a process normally implies effective brownstock washing and a closed screen room, which will reduce colour discharges by a up to a further 50%, depending on the original losses from the brownstock washers.

Several external effluent treatment techniques have been developed to decrease the colour in bleach kraft mill effluents, (Rush and Shanon 1976), but we are unaware of any that have remained in operation for more than a few years, except one very site specific system in British Columbia.

3.3.8 Organochlorine Compounds

Whenever chlorine or chlorine compounds are used to bleach pulp, a vast variety of organochlorines are created, including the dioxins which attracted so much media attention in 1987. The majority of these substances are formed in the first chlorination stage of the bleach plant, and appear in both the chlorination stage and the subsequent caustic extraction filtrates (refer to Figure 3.2).

There are very few data published on the chlorinated dioxin and furan content of bleached kraft mill waste waters, so many current assumptions are based on Amendola (1987) and on Consolidated Papers (1987). These authors found that 2378 TCDD was discharged by all the bleach plants tested, except from one

bleach line at Consolidated which used oxygen delignification. We have been advised of unpublished data on analysis of waste waters from about 20 bleach plants around North America, and some dioxins and furans, including 2378 TCDD, were found in all cases, so we are forced to assume that most bleached kraft mills discharge

Typical quantities of chlorinated organic compounds in bleach plant effluents are 5 kg/t pulp or more. Biological treatment decreases this, but some compounds (such as chlorinated guaiacols) are unaffected. The quantity of chlorinated organic compounds generated is roughly in proportion to the amount of chlorine used to bleach the pulp, and most of the potential measures for reduction of organochlorine discharges are based on replacing the chlorine with other bleaching agents or processes.

Many of the lower molecular weight (under 1000) chlorinated organic compounds are acutely toxic to fish according to the types of functional groups and the degree of chlorine substitution on the aromatic ring. They are also moderately bioaccumulative in fish and are fairly resistant to conventional biological treatment processes. Compounds identified thus far account for only a small fraction (less than 10%) of total organically bound chlorine (McKague 1988).

Organochlorines are discussed in depth in sections 9 and 10, and methods of reducing discharges in several parts of Section 3.2, 3.7 and 4.8. Current organochlorine discharges in Ontario are presented in Section 6.

3.3.9 Sulphur Dioxide Treatment of Chlorination Effluent

The effluent from the bleach plant chlorination stage is one of the principal sources of toxicity to fish in most bleached kraft pulp mills. It has been shown that if residual chlorine is stripped from the chlorination stage effluent, the pH raised to 5.5 and about 0.02% sulphur dioxide added, the effluent toxicity will be substantially decreased or eliminated. The work performed indicates that the performance of this treatment process varies between mills and wood species, as with most effluent treatment processes, and that it is essential that the unbleached pulp be washed effectively prior to bleaching. This process was used successfully for a short time in the 1960's, and received renewed attention in research in the early 1980's. (Betts and Wilson 1966, Donnini 1981, 1983a, Donnini et al. 1985)

3.3.10 Substitution of Chlorine Dioxide for Chlorine

SUMMARY Chlorine Dioxide can be used in place of most of the elemental chlorine to bleach pulp. This practice improves effluent and pulp quality. For most mills it is the simplest, most widely proven and most economical way of reducing organochlorines. Relative to a mill with neither oxygen delignification nor chlorine dioxide substitution, the latter can reduce organochlorine discharges by up to approximately 50%, if a very high proportion of the chlorine is replaced, while oxygen delignification would achieve about 40% reduction in the same mill.

It is common practice for mills to substitute small quantities (5%-15%) of chlorine dioxide in the first (chlorination) stage of the bleach plant. The advantages are mostly concerned with improvements in pulp quality, but since 1 kg of Chlorine Dioxide can replace approximately 2.63 kg chlorine, there is a net reduction in the amount of chlorine used, and a reduction in discharges of organochlorines.

Chlorine dioxide substitution is defined as the percentage of "equivalent chlorine" used in the form of chlorine dioxide in the chlorination stage. For example, a bleach plant which does not practice chlorine dioxide substitution may use 60 kg of elemental chlorine in the first chlorination stage per tonne pulp produced. If it converted to 30% substitution, then the elemental chlorine charge could drop to 42 kg/t pulp, augmented by 6.84 kg/t chlorine dioxide. The foregoing example assumes a constant replacement factor of 2.63, which is common practice for rapid calculations. However, many authors, including du Manoir (1982) have shown that delignification efficiency improves as the degree of substitution increases, up to about 4:1 in some cases. Calculations in this report take account of this improvement.

Figure 3.5 shows the effect of substituting up to 70% of the chlorine dioxide in a typical softwood bleach plant on organochlorine discharge. The relative chemical consumptions were calculated according to the substitution factors developed by du Manoir (McDonough 1985), with some modifications from the author's experience to allow for the less than ideal design of many of Ontario's bleach plants. The relative cost of bleaching chemicals is also shown, based on the chemical costs in Table 3.5 which are representative of the current situation in Ontario.

Table 3.5 Typical prices of bleaching chemicals, $/tonne for mill site. [4]

Chlorine	$275
Caustic	$280
Oxygen (by truck)	$150
Oxygen (on-site generation)[5]	$80
Chlorine Dioxide (on site generation)	$1000

The highest level of chlorine dioxide substitution with any significant operating experience is 70%, but laboratory work and limited mill experience shows that levels up to 100% are practicable in some cases. Substitution up to about 50% has little impact on chemical costs, but higher levels can increase costs markedly.

Acute toxicity (the traditional lethal test) may or may not be improved much by high chlorine dioxide substitution, the main point is not to reduce acute toxicity, but to decrease the production of persistent organochlorine toxicants, which have more subtle effects.

One benefit of ClO_2 substitution is that mutagenicity drops off, until at 100% substitution the mutagenicity is no higher than in control tests (Refer also to further discussion in Section 8.5 on mutagenicity.)

4 Costs are typical late 1987 prices in Ontario, and are higher than in many other pulp producing regions, which tends to make oxygen delignification more economically attractive in Ontario than elsewhere

5 On-site oxygen generation becomes practical for over about ten tonnes/day as would be used for oxygen delignification. Several competing suppliers offer oxygen at this price, on an "over the fence" contract, whereby the price includes financing, building and operating the oxygen generator, and providing back-up by truck.

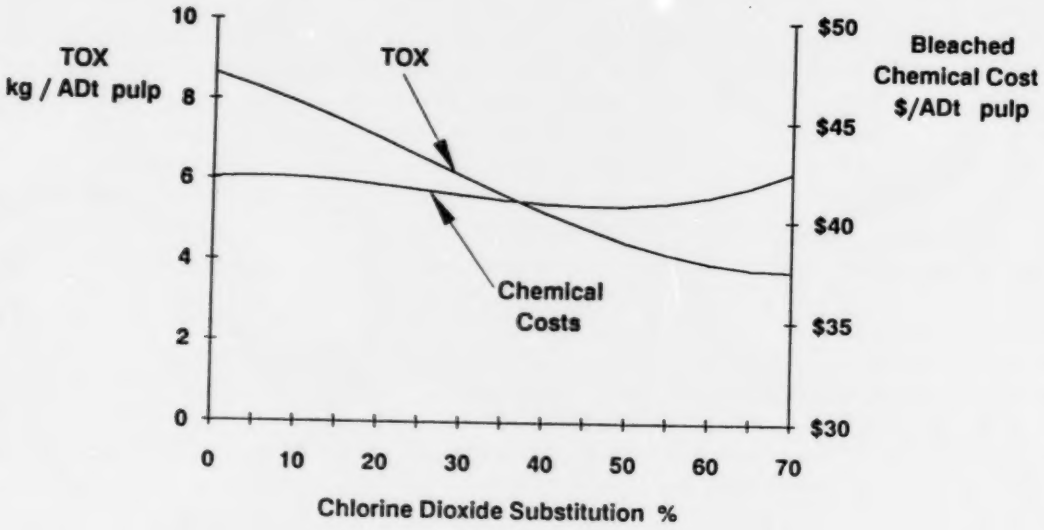


Figure 3.5 Effect of chlorine dioxide substitution on organochlorine discharges. Calculated by authors, based on Germgård (1983) and du Manoir (1982)

Opinions are divided as to whether the acute lethality of combined bleach plant effluent may or may not change greatly with ClO_2 substitution, even though water from individual stages may show encouraging drops in toxicity. Various results in the literature are contradictory. Sometimes the toxicity does not change greatly (Donnini 1983b, Voss and Wearing 1981). In other research, acute lethality was essentially eliminated by substituting 55%, 70%, or 100% ClO_2 (Betts and Wilson 1966), or toxicity was reduced in all trials in which ClO_2 replaced some chlorine (Wong et al. 1978). Similarly the toxicity emission factor (TEF, or Toxic Units x m^3 effluent per tonne of pulp) was reduced by half with 100% substitution (Nikki and Korhonen 1983). A few authors have stated that under some circumstances, toxicity may increase with greater ClO_2 substitution. Kutney et al. (1985) showed that the amount of toxicity (TEF) in the CEDED combined effluent from softwood processing, increased from 120 with no ClO_2 to 180 with 70% ClO_2 substitution. The change was even more marked for kraft hardwood, the TEF rising from 160 to 350.

The technology and equipment required to modify and operate bleach plants at high chlorine dioxide substitution have been quite well known for well over ten years. McDonough (1985) edited a review of then current literature. Pryke (1988) described the current technology of using chlorine dioxide, and indicated varying values for the reduction in AOX which were achieved by high chlorine dioxide substitution. In his verbal presentation he advised that the data on AOX were questionable due to poor lab work, so we have discounted them, and refer readers to his paper as a recent description of the technology.

The **capital installation** required to increase chlorine dioxide substitution depends mostly on the capacity of the mill's existing chlorine dioxide generator, since the modifications required to the bleach plant itself are minor or nil.

Chlorine dioxide is an unstable chemical which cannot be transported effectively, so all mills prepare it on site from sodium chlorate and one or more reducing agents such as sulphur dioxide or methanol. The capital cost of increasing chlorine dioxide generating capacity typically varies from $100,000 to $200,000/daily tonne additional chlorine dioxide required. All Ontario mills, except perhaps at Thunder Bay, Cornwall and Espanola, would probably have to install such additional capacity to utilise chlorine dioxide substitution to the optimum environmental level.

All the current chlorine dioxide processes affect the **overall mill chemical balance** because they produce inorganic by-product streams which consist of sodium and sulphur in various forms, primarily of sodium sulphate and sulphuric acid. In mills using low chlorine dioxide substitution in the bleach plant, the quantities of chlorine dioxide required are such that all these by-products can be used for make-up to the pulping chemical cycle as shown in Figure 3.2.

However, when high chlorine dioxide substitution is used, it may be impossible to use all of the by-products. Although it is conceptually possible to sell the excess by-products, this is rarely done, due to various practical difficulties, so they must be discharged to the sewer. We do not consider the discharge of unusable chlorine dioxide generator by-products (sodium sulphate and sulphuric acid) to be of any environmental significance . However, the fact that the mill cannot take credit for these chemicals raises the effective cost of chlorine dioxide, which is reflected in the estimated cost of the latter that we have used in this report.

There are a number of ways of expanding the capacity of the on-site chlorine dioxide plants and the technology is well known and available from several competing suppliers. Gray and Axegard (1987) summarise current options, and include the relevant chemical balances and costs.

3.3.11 Alkali/Oxygen Extraction

The use of relatively small quantities of oxygen in the conventional caustic extraction stage, as shown in Figure 3.2, has been shown to have some advantages in reducing the consumption of chlorine dioxide in later bleaching stages. This has a minor impact on effluent quality, but since it decreases the input of chlorine to the system, it reduces the discharge of chlorinated organic compounds by about 15%.

In this process variation, the gaseous oxygen is mixed with the pulp and sodium hydroxide immediately prior to the caustic extraction (E) stage of a conventional CEDED or DcEDED (or similar) bleaching process. The gas is introduced near the bottom of the extraction tower, which is typically about 20m high, where the hydrostatic pressure is about 200 kPa, and the oxygen reacts with pulp almost immediately (Nonni 1985, Massey and Nay 1984).

Many Canadian mills have installed permanent equipment for its application, including most of the bleaching lines in Ontario.

3.3.12 Oxygen Delignification (Bleaching)

SUMMARY Prior to 1970, virtually all chemical pulp bleach plants were based entirely on the use of chlorine and chlorine compounds. However, since the early 1970's, oxygen has partially replaced chlorine in many European mills, as well as a few US mills and one Canadian mill. The principal reasons for the installation of most oxygen delignification systems are reduction of chemical costs and improvement of effluent quality. The oxygen filtrate is recycled to the chemical recovery system in most cases, thus permitting incineration of the compounds which give rise to the BOD, toxicity, organochlorines and colour in the bleach plant effluent.

The terms **"oxygen delignification"** and **"oxygen bleaching"** are often used interchangeably to refer to the process discussed in this section. The term "Oxygen Bleaching" is also sometimes used to refer to the addition of elemental oxygen to the caustic extraction stage, described in Section 3.3.11 above.

The **Kappa Number** is a widely used test (TAPPI 1988) which has been used as the measure of the content of ligneous and related organic material for most mill operations and research work in this field. The Permanganate number (or "K Number") is also used for this purpose.

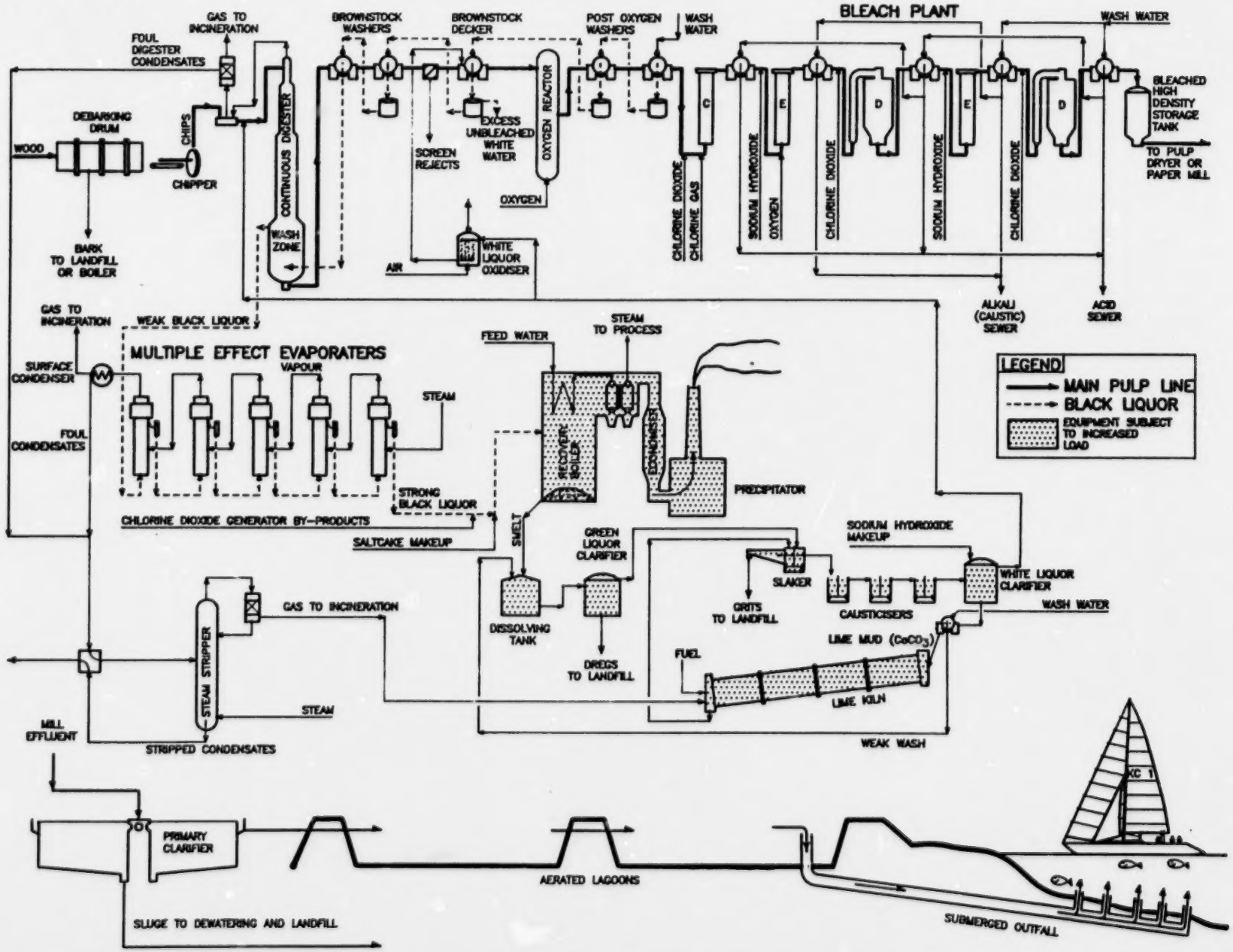
In practice, oxygen delignification can be used to reduce the Kappa number of the kraft pulp by about 50%, which results in a reduction of about 40% in the quantity of chlorinated organic compounds generated in subsequent chlorine based bleaching processes.

The raw effluent from systems using oxygen is generally highly coloured and has somewhat higher BOD than chlorination bleaching effluent, so the maximum environmental benefits are realised only if the filtrate from the oxygen stage is recycled to the chemical recovery system, which is universal practice. However, the efficacy of oxygen delignification in reducing the discharge of chlorinated organic materials is not dependent on such recycle. The installation of an oxygen delignification will allow most bleached kraft mills to reduce bleach plant BOD discharges by approximately 50% and colour by 60% (McCubbin 1983). Discharges of organochlorines will be reduced by approximately 35% - 50% (Norström 1987).

There is some information on reduction of acute toxicity by oxygen delignification. An overall 50% reduction in amount of toxicity (i.e. Toxic Units per tonne of pulp) has been claimed by Arhippainen and Malinen (1987), and reductions of 50% to 70% in acute toxicity to fish are listed by Idner (1987). There was definite reduction of toxicity in Microtox tests, in which the toxic concentration was raised from 4%, for bleach plant effluents without O_2, to 33% with O_2 pretreatment (Germgård et al. 1985). In the same research project, mutagenicity of chlorination effluent was reduced from a response-level of 600 to levels of 20-40 with O_2 delignification, a major reduction. Some comparisons do not show such great advantages, for example effluents collected from mills with and without oxygen delignification did not yield clear differences in toxicity (IPK 1982). The laboratory tests of bleaching carried out by Wong et al. (1978) were inconclusive about toxicity reduction by oxygen delignification, since the authors state that much of the measured toxicity was caused by residual chlorine.

Figure 3.6 shows a complete bleached kraft mill flowsheet similar to that shown earlier in Figure 3.2, but with an oxygen delignification system inserted between the brownstock screens and the bleach plant. Equipment which will experience higher loading is due to the oxygen delignification system is shaded.

Figure 3.6 Mill Flowsheet with Oxygen Delignification



Note that the organic material removed from the pulp in the oxygen delignification stage is routed to the recovery boiler, and that it does not contain chlorinated organic substances, since chlorine is added to the pulp only after the oxygen stage.

It is generally recommended that the brownstock be washed to a soda loss of below 12 kg sodium sulfate per tonne to avoid excessive oxygen consumption and heat generation in the oxygen reactor, and washing to a lower soda loss value is desirable. This is not at all difficult technically, but the costs and benefits of improved brownstock washing have to be included in any analysis of retrofitting an oxygen delignification system to an existing mill.

Most mills which have installed oxygen delignification systems have also taken steps to ensure that the preceding screening operations operate on a closed cycle, (a "closed screenroom"). While this is desirable for the reduction of BOD and colour, it results in the maximum load on the mill's recovery boiler. Where it is desired to use oxygen delignification to reduce the discharge of chlorinated organic compounds, it is technically feasible to operate with an open screen room to reduce the amount of organic material returned to the recovery boiler.

The economics of oxygen bleaching are dependent on local prices for oxygen relative to chlorine and the chemicals for on-site manufacture of chlorine dioxide. The published data indicates that the operating costs for bleached kraft mills incorporating oxygen delignification stages are lower than for the traditional chlorine based systems. The present authors have calculated that the average Ontario softwood kraft mill can save $12/t pulp by installing oxygen delignification systems, based on Ontario chemical prices prevailing in late 1987. The savings vary according to local conditions, and depend mostly on the effectiveness of the existing bleach plant in producing satisfactory quality pulp in the quantities with minimal chemical consumption. The chemical savings were calculated individually when estimating costs for Section 12 of this report.

Oxygen delignification is being used to produce a variety of pulp grades, and there are about 40 oxygen delignification systems operating in kraft mills around the world, with another dozen under construction, as shown in the following table. When oxygen delignification was introduced in the early 1970's, the regulations pertaining to new mill construction in most parts of the US and for new Canadian mills were such that a biological treatment system was necessary to comply with the BOD and/or toxicity criteria, so that the environmental advantage of using the oxygen process was limited to a modest marginal reduction in effluent treatment costs. However, many Scandinavian mills were permitted to operate without biological treatment systems, provided that they installed oxygen delignification stages, so it was more economically attractive for them to do so than for North American mills.

There are two principal oxygen delignification processes, as discussed below, and the implications of installing them in an existing mill are discussed in Section 3.7

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6 "Soda loss" is a misnomer, since the soda remaining in the pulp will eventually be recycled from the oxygen stage washers to the recovery system. However, the term is widely used, for historical reasons. The real significance of the "soda loss" is that the content of ligneous, organic material is roughly proportional to the sodium salt content, and it is this organic material which is liable to be converted to chlorinated organic compounds whenever bleaching agents containing chlorine are reacted with the pulp.

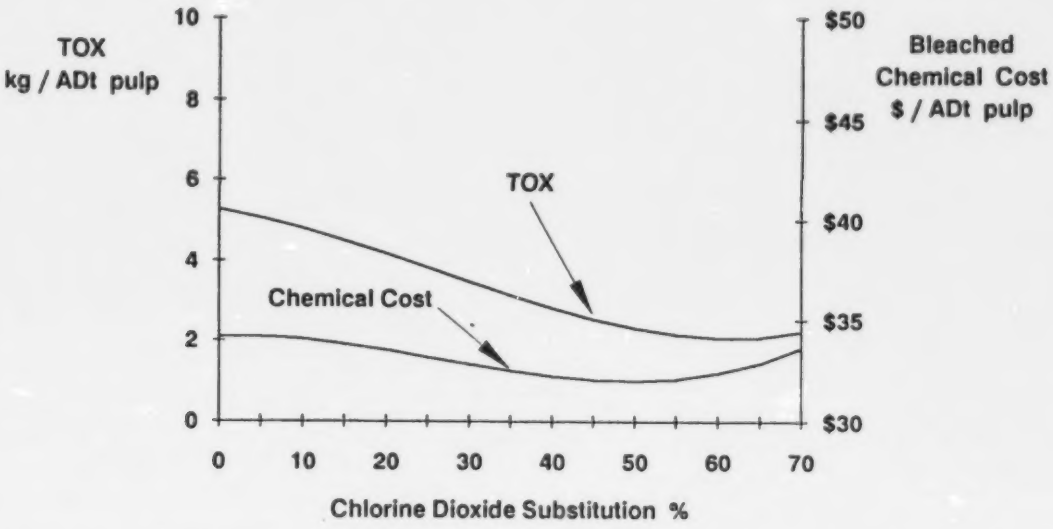

Figure 3.7 Effect of oxygen delignification on organochlorine discharges for various levels of chlorine dioxide substitution.; Calculations by authors, based on Germgård (1983) and du Manoir(1982).

3.3.13 High Consistency Oxygen Delignification

In high consistency oxygen delignification systems the washed, unbleached pulp is dewatered to 25 - 30% consistency in a press and fed to a pressurised reactor where gaseous oxygen is introduced. Sodium hydroxide is added to the pulp to control the pH to about 10, and about 1.4 kg magnesium salt ("viscosity protector") per tonne pulp is also added to control the tendency of oxygen to attack the cellulose fibres. The reactor is a pressure vessel with an internal fluffer and/or agitator to disperse the high consistency pulp to ensure even contact with oxygen. The gaseous oxygen is fed to the reactor directly, and a small bleed to atmosphere is maintained to purge air and small quantities of carbon monoxide. After discharge from the reactor, the pulp is washed, either on a drum washer or a diffusion washer, in a similar manner to that used for the unbleached stock from the digester. The filtrate from this washing stage contains about 50% of the BOD, toxic material and coloured material which would be discharged from a conventional chlorine based bleach plant. The only oxygen delignification systems operating in Canada, at Espanola, use the high consistency process.

3.3.14 Medium Consistency Oxygen Delignification

Since the first commercial scale high consistency oxygen delignification systems were commissioned in the early 1970's, there has been considerable evolutionary development, as is characteristic of any new technology. Most of this has had little effect on the environmental protection aspects of the process, but the demonstration of the feasibility of performing the delignification at medium consistency, 10% to 15%, is important in that it allows the construction of oxygen delignification systems at lower capital costs than for the high consistency systems. This process variation is described by Markham and Magnotta (1981) and at the time of writing the suppliers of almost all of the operating high consistency oxygen bleaching systems recommend the medium consistency approach for most applications. The medium consistency process must now be considered as the conventional way of delignifying pulp with oxygen, and it seems unlikely that any further high consistency systems will be installed

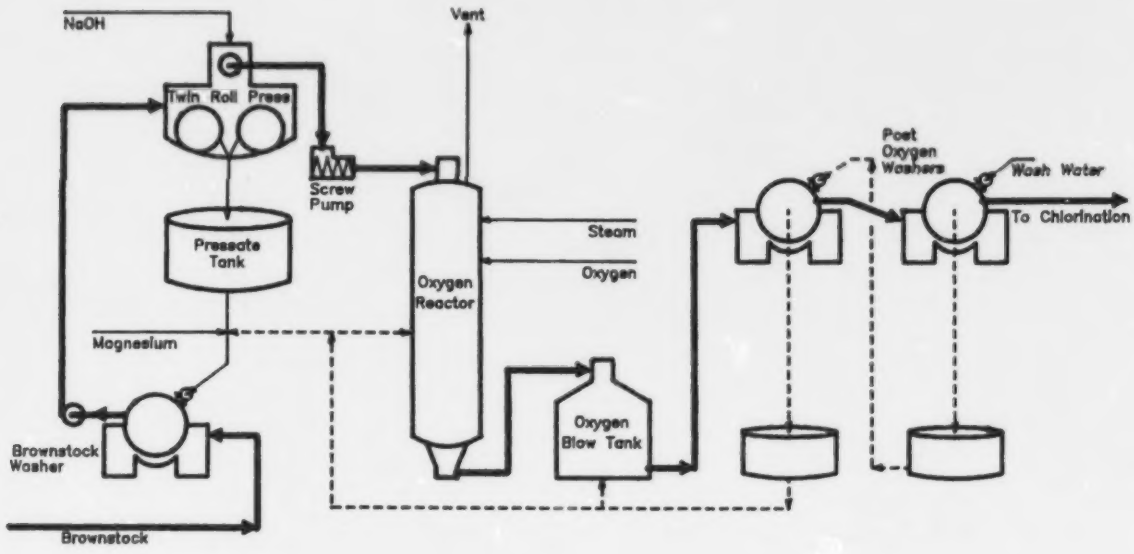

Figure 3.8 High consistency oxygen delignification system.

The process flowsheet is presented in Figure 3.9 where the lines containing residual organic substances removed from the pulp are shown dashed. . The essential equipment difference is that the pulp can be dewatered to a suitable consistency by a conventional brownstock decker, which already exists in many mills, instead of using a press. At the consistencies used, the pulp is less liable to be degraded by locally high oxygen application, and the potential risk of fire in the reactor is eliminated. The cost of magnesium salt for viscosity protection is reduced or even eliminated.

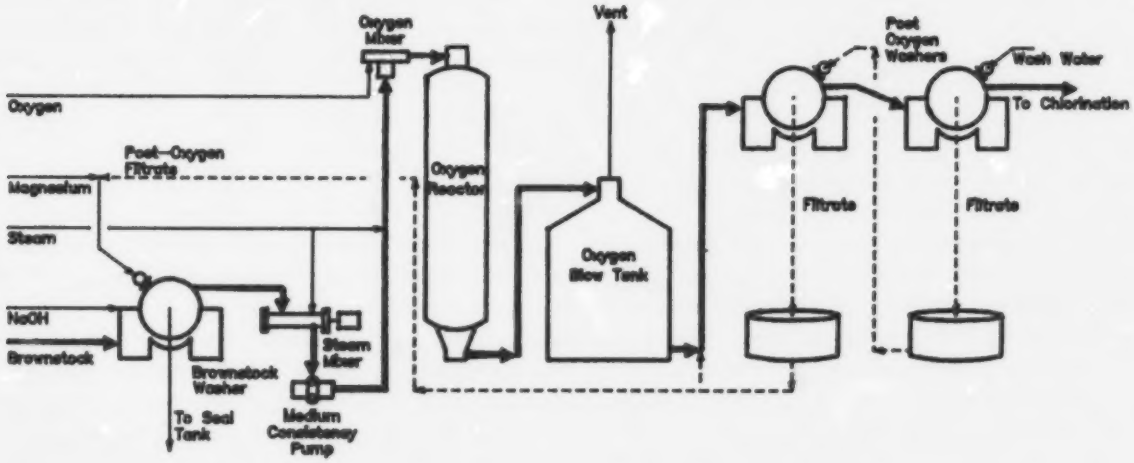

Figure 3.9 Medium consistency oxygen delignification

3.3.15 Problems with Oxygen Delignification

With the evident environmental advantages that oxygen delignification offers to all mills, and economic advantages to many, one is forced to wonder why it has not become normal practice in Ontario. The *following paragraphs address the commonly quoted* reasons for not installing oxygen delignification systems in kraft mills.

"Pulp quality is inadequate for market grade mills, particularly with respect to brightness and strength." This is not so, as demonstrated by the apparent success of the 20 or so market kraft mills operating worldwide, (Refer to Figure 3.10 and Table 3.6) as well as several more under construction. E.B. Eddy in Ontario has been selling their oxygen-delignified pulp for many years, and discussions we have had with pulp sales personnel with experience in handling oxygen delignified pulp indicate that customers have no preference for or against it.

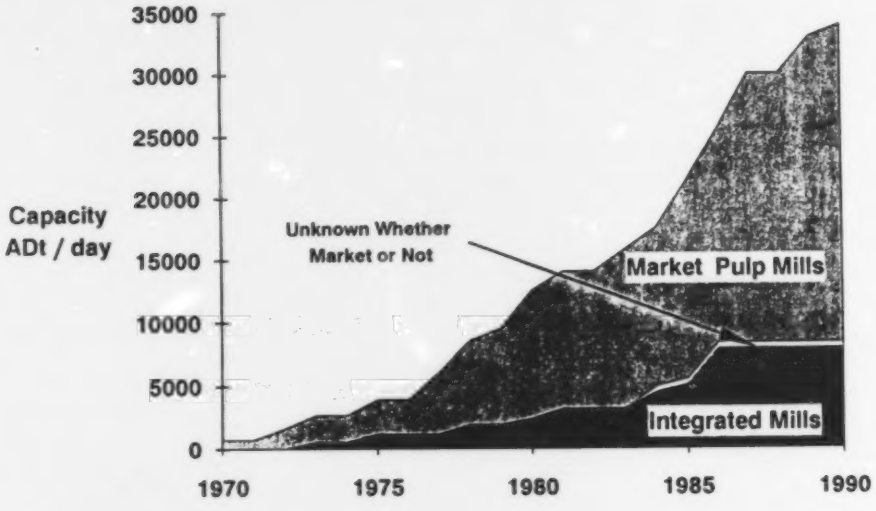

Figure 3.10 Oxygen delignification installations.

Brightness stability is an important characteristic of market pulps, and oxygen delignified pulp is claimed to suffer less brightness reversion than traditionally processed pulps. Our own contacts with pulp users elicited the opinion that oxygen delignified pulps are equal to, or marginally better than those from mills not using oxygen delignification. In this respect Croon (1971) and David et al (1976) reported improved brightness stability in oxygen delignified pulps.

The quality of oxygen delignified pulps has been discussed frequently in the literature over the past twenty years and the following authors have concluded that the **strength** of these pulps is comparable to traditional kraft pulps (Croon and Andrews 1971, Jamieson and Smedman 1973, Schleinkofer 1982 & 1983, Liebergott et al 1985, Munro 1987, Tench and Harper 1987).

Table 3.6 Installations of oxygen delignification systems.

Company	Location		Install Year	Capacity ADMTPD	Consist.	Wood Type
Sappi	Enstra	S. Africa	1970	200	high	soft
Billerud	Gruvon	Sweden	1972	500	high	soft
Chesapeake	West Point	Virginia	1972	550	high	hard
Munksjo	Aspa	Sweden	1973	380	high	soft
Cellulose d'Aquitaine	St-Gaudens	France	1973	500	high	hard
Daishowa	Shiraoi	Japan	1975	550	high	hard
Jujo Paper	Kushiro	Japan	1975	600	high	soft
Stora Kopparberg	Skutskaer	Sweden	1977	650	high	soft
MoDoCell	Husum	Sweden	1977	1,000	high	soft
Eddy Forest Products	Espanola	Ontario	1977	500	high	soft
Stora Kopparberg	Skutskaer	Sweden	1978	650	high	soft
Noorlands Skogsagares Cell.	Vallvik	Sweden	1978	600	high	soft
ZCP	Kwidzyn	Poland	1978	600	high	soft
Sappi	Enstra	S. Africa	1978	500	high	hard
Ust	Illimsk	USSR	1979	800	high	soft
Svenska Cellulosa	Ostrand	Sweden	1980	1,000	high	both
Eddy Forest Products	Espanola	Ontario	1980	500	high	hard
Procter & Gamble	Oglethorpe	Georgia	1980	1,000	high	soft
Consolidated Paper	Wis. Rapids	Wisconsin	1980	450	medium	hard
Sodra Skogsagarna	Monsteras	Sweden	1981	1,000	high	both
Union Camp Corporation	Franklin	Virginia	1981	800	high	hard
Tofte Industrier	Tofte	Norway	1983	700	medium	soft
Kopparfors	Norrsundet	Sweden	1983	1,000	high	both
Korsnas	Marmaverken	Sweden	1983	100	medium	
Zellstoff	Polser	Austria	1984	630	medium	soft
Union Camp Corporation	Eastover	S. Carolina	1984	650	high	both
Taio Seishi Paper	Mishima	Japan	1984	665	medium	hard
V/O Prommash	Svetogorsk	USSR	1985	455	medium	hard
Sappi	Ngodwana	S. Africa	1985	575	high	soft
Oji Paper	Tomakomai	Japan	1985	550	medium	soft
Cellulose des Ardennes	Rouvroy	Belgium	1985	520	medium	hard
Sodra Skogsagarna	Varobacka	Sweden	1985	950	medium	soft
Fiskeby	Skaerblacka	Sweden	1985	510	medium	both
Champion Int'l.	Pensacola	Florida	1986	730	medium	hard
Chuetsu Pulp Kogio.K.K	Sendai	Japan	1986	550	medium	both
Taio Seishi Paper	Mishima	Japan	1986	525	medium	soft
Daishowa	Suzukawa	Japan	1986	620	medium	hard
Oji Paper	Ebetsu	Japan	1986	650	medium	both
Daishowa	Shiraoi	Japan	1986	400	medium	hard
Hokuetsu Paper	Niigata	Japan	1986	480	medium	hard
Mitsubishi	Shirakawa	Japan	1986	300	medium	hard
Champion Int'l	Pensacola	Florida	1986	560	medium	hard
Kishu Paper	Shingu	Japan	1987		medium	hard
Champion International	Hinton	Canada	1987	1,300	medium	soft
Korsnas Marma	Galve	Sweden	1987	1,050	medium	
Oy Schauman	Jakobstad	Finland	1987	900	medium	soft
Chung Hwa	Hualien Hsien	Taiwan	1987	445	medium	
Chung Hwa	Hualien Hsien	Taiwan	1987	445	medium	
Sodra Skogsagarna	Morrum	Sweden	1989	420	medium	soft
Sodra Skogsagarna	Morrum	Sweden	1989	700	medium	hard
Susano de Papel e Celluose	Suzano	Brazil	1989	1,365	medium	hard
Diashowa	Peace River	Alberta	1990	1000	medium	soft
Canfor	Port Mellon	B.C.	1990	1,000	medium	soft

"The increase in dissolved solids recovered would necessitate a **new recovery boiler** at a capital cost of fifty to one hundred million dollars." If the mill recovery boiler is the production bottleneck, there are several proven techniques for increasing its effective capacity without incurring these high capital costs. They all have some capital and/or operating cost, which must be considered in the overall economic

evaluation of installing an oxygen delignification system, but the costs are either relatively modest, as is the case for anthraquinone, or else they bring additional benefits, as in the case of black liquor oxidation. Solutions to this problem discussed elsewhere in this report include:

Anthraquinone addition can reduce boiler load by 7% as discussed in Section 3.2.5;
Black liquor oxidation can reduce boiler load up to 2% as discussed in Section 3.5.3;
Various aspects of recovery boiler capacity are discussed in Section 3.5; and
Soap disposal is discussed in Section 3.4.5. Up to about 10% reduction in boiler load can be achieved by soap removal and disposal by conversion to tall oil, sale or incineration elsewhere, but the potential of using the approach in Ontario mills is limited, since many do so already.

"Oxygen delignification systems are **difficult to operate**." The number of operating installations demonstrates that any difficulties are surmountable, particularly in view of the number of companies who have purchased second and third systems after initial operating experience.

"The **capital cost of oxygen delignification is excessive**." As discussed in Section 12, the return on investment in oxygen delignification is above the hurdle cost of capital.

"Oxygen is **hazardous**." While there is a potential fire hazard in high consistency oxygen delignification systems, they have a good track record with respect to safety. Some systems are approaching 20 years old. Medium consistency systems operate in the liquid phase, and are no more hazardous than other process equipment used widely in the industry.

"**Future chemical costs are unknown.**" This is true, but it is also true for other industrial chemicals. Oxygen is a major industrial chemical supplied under competitive conditions and thus the long run price will not rise above the cost of production. The latter depends to a large extent on the price of electrical energy, as do all the chlorine based bleaching chemicals. The energy requirement of the various bleaching chemicals is summarised in Table 3.7

Table 3.7 Energy content in some bleach chemicals and for chemicals in bleaching sequences.;(Croon 1983)

Individual chemicals	
Oxygen	0.5 kWh/kg
Chlorine	1.7 kWh/kg
Sodium hydroxide	1.7 kWh/kg
Chlorine dioxide(active, Cl_2)	5.0 kWh/kg
Sodium Hypochlorite	3.004 kWh/kg
Bleaching sequence	
C/D-E-D-E-D	425. kWh/ADt
O-C/D-E-D-E-D	290. kWh/ADt
O-C/D-Eo-D	290. kWh/ADt

If we assume that the energy prices will rise faster than other costs in the long term, then oxygen costs are less likely to rise than the costs of chlorine based bleaching agents and sodium hydroxide.

"If all the mills converted to oxygen delignification, **where would we get our caustic**". This is in reference to the fact that (sodium hydroxide (caustic) must be produced in a fixed ratio to chlorine by any viable process, and the pulp industry normally purchases these two chemicals in stochiometric ratio, while an oxygen stage uses sodium hydroxide but no chlorine. The solution is for mills using oxygen delignification to use oxidised white liquor for alkali supply to the oxygen stage, as shown in figure 3.6. This is universal practice in existing installations.

It should be noted that the pulp industry purchases only about one third of the chlorine manufactured in Canada, whereas in 1970 is was the predominant user of chlorine.

3.3.16 Washing Following Oxygen Delignification

If the potential of the oxygen delignification stage to reduce the quantity of chlorinated organic materials in the effluent is to be realised, then it is essential to minimise the quantity of organics which pass forward to the subsequent chlorine bleaching stages with the pulp. There has been a recent trend toward installing two washing stages after the oxygen stage, which is environmentally desirable, but incurs capital and operating costs. There are at least two mills operating with three stages of washing after the oxygen delignification stage (Tench and Harper 1987)

There are various references in the literature to the need for "good" washing following oxygen delignification, but few data. It is technically feasible to limit the loss of sodium to the subsequent chlorine based bleaching process to under 10 kg organics per tonne pulp, but not necessarily economic.

Figure 3.6 shows a kraft mill similar to the traditional mill shown in Figure 3.2, but with an oxygen delignification system installed. Conventional practice would be to install two post oxygen washers, and recirculate the filtrate as shown. However, if the filtrate from the second post oxygen washer is sewered directly, and fresh water used as shower water on the first washer, then the flow of organics into the chlorine stage would be reduced by about half, at the cost of some increase in mill effluent BOD, and reduction in bleach chemical cost. This is not practiced in any mill that we know of at present, but is under study, and serves to illustrate one of the classic chemical engineering trade-offs that have not yet been optimised in current systems. Further improvements will no doubt emerge as engineering experience is gained in minimising organochlorine discharges.

3.3.17 Bleaching Following Oxygen Delignification

The most commonly used sequence is OCdEDED, where about half of the total delignification is accomplished in the oxygen stage, resulting in 50% of the BOD and at least 60% of the colour and toxic material in the effluent being recycled to the recovery furnace. Where the Cd stage utilises high chlorine dioxide substitution (over 20%), the effluent colour and toxicity are reported to be further decreased, as is the total chlorine content of the effluent, facilitating any recycle to the recovery furnace.

Other, simplified, sequences have been proposed, and are attaining limited commercial status, such as ODcEoD where the E stage uses alkali/oxygen extraction as mentioned previously. Such "short" sequences generally have lower capital costs and lower effluent flows than the conventional sequences, and although further operating experience is required to demonstrate whether or not they will be commercially successful. The potential of using short sequences in some Ontario mills appears good, which would result in a relatively low cost oxygen delignification system.

The filtrates from washing after the first chlorine (Cd or Dc) stage contain chlorides so it is impractical to recycle these effluents to the recovery furnace along with the oxygen stage filtrates.

3.4 Recovery of Pulping Chemicals

SUMMARY The spent pulping liquor removed from the pulp in the washing stages contains virtually all the original cooking chemicals and organic material removed from the wood. The quantity of total dissolved material depends principally on the pulping yield and is typically 1500 to 1800 kg/t for kraft pulp. All kraft mills in Ontario have chemical recovery operations, using the technology described in this section. Typically 96-99.5% of the spent liquor is recovered, and the rest becomes part of the mill effluent. The efficiency and reliability of the chemical recovery system has a major impact on all effluent parameters except those related to chlorinated organics.

3.4.1 Process Description

The fundamental recovery process cycle in which the cooking chemicals are regenerated and the organic residues burned to produce energy for process and power is shown in figures 3.1 and 3.2.

The weak black liquor removed from the pulp by the brown stock washers is concentrated in a steam heated multiple effect evaporator to about 50% dry solids.

This liquor is further concentrated to about 65% solids concentration either by direct contact with recovery furnace flue gas or indirectly in a forced circulation steam heated evaporator, generally known as a concentrator.

The strong black liquor is then burned in a recovery furnace. The organic matter burns providing heat for steam generation while the sodium/sulphur salts accumulate in the hearth of the furnace as a molten smelt. At the high temperatures and controlled conditions employed, the Na_2SO_4 added to the black liquor as make-up for sodium and sulphur losses is reduced to Na_2S as follows:

$$Na_2SO_4 + 2C \xrightarrow[840^\circ C]{} Na_2S + 2CO_2$$

The molten smelt, composed mainly of Na_2S, Na_2CO_3 and some unconverted Na_2SO_4, flows by gravity from the furnace and is mixed with weak wash, the filtrate from lime washing, in the dissolving tanks. The greenish colour of the molten salts is imparted to the water mixture and thus it is universally referred to as green liquor.

The green liquor is pumped to a green liquor clarifier where carbonaceous ash residues, and other impurities are removed by sedimentation. The settled residue, known as green liquor dregs, or simply dregs, is washed to remove soluble sodium salts. The dissolved salts are returned to the system while the dregs are either hauled away for landfill or discharged to the sewer. Typically about 0.5 kg dregs are generated per tonne pulp.

The clarified green liquor is them routed to the causticising system where calcium hydroxide is added, in the slaker, to convert the sodium carbonate to sodium hydroxide according to the reaction below:

$$Ca(OH)_2 + Na_2CO_3 \text{ --------> } 2NaOH + CaCO_3$$

The reaction, which is rather slow, begins in the slaker and is completed in the causticisers, which are agitated retention tanks immediately downstream of the slaker. The calcium carbonate formed from the reaction is quite insoluble and is settled out of solution in the white liquor clarifier. The clarified solution which overflows contains the two major active cooking chemicals, Na_2S and NaOH. This liquor is called white liquor and is ready for re-use in the digester.

The calcium carbonate removed from the white liquor clarifier is pumped to a lime mud filter where it is thickened and washed to recover entrained sodium salts. The thickened $CaCO_3$ is then calcined in a direct fired lime kiln, which converts it to calcium oxide as follows.

$$CaCO_3 + \text{heat} \text{ --------> } CaO + CO_2$$

The CaO produced is recovered and used in the slaker.

The only solid wastes are the slakers grits which are non-reactive lime and inert mineral matter and the green liquor dregs consisting of carbon, ash and some sodium.

The principal organic discharge in the chemical recovery system is the evaporator condensate, discussed below.

The total flow of organic material from the pulp washers through to the recovery furnace should be noted, since it is equivalent to about 300 kg BOD per tonne pulp, and contains large quantities of resin acids and other material toxic to fish, but no chlorinated organic compounds. In some internal recycle streams, the flow or organics can be up to ten times greater so it is clear that even a very small percentage loss of this flow, which passes through a variety of complex equipment, would represent a substantial BOD load on the waste treatment plant or receiving water.

Table 3.8 Typical mass and energy flows for a 750 ADt/d bleached kraft pulp mill.

	Steam t/hr	Water lpm	Dry Solids kg/h	BOD kg/h
Wood into digester	-	1100	58500	-
White liquor into digester (Na2O)	-	2450	9800	1960
Pulp wash water flow	-	5150	0	0
Steam to digester	57	-	-	-
Weak black liquor to evaporators	-	4950	58250	8700
Steam to evaporators	71	-	-	-
Evaporator condensate	-	4400	-	400
Strong black liquor to furnace	-	550	59000	8300
Steam produced	138	-	-	-
Saltcake make-up	-	0	700	0
Green liquor dregs	-	7	20	3
Lime feed to slaker	-	0	7000	0
Slaker grits	-	3	50	0
Lime mud flow to thickener	-	280	11200	200

Note: Inorganic chemicals such as white liquor and green liquor exert a BOD due to chemical oxidation of sodium sulphide under the conditions of a BOD test.

3.4.2 Evaporators

The weak black liquor is received at the recovery department at a concentration of about 14 to 18% solids, and this concentration must be raised substantially by evaporation before it can be fed to the recovery furnace. Specially designed vertical shell and tube heat exchangers called evaporators are normally used for this evaporation process, arranged generally as shown in Figure 3.2.

Volatile organic compounds, principally methanol, condense in the shells of the surface condenser and the evaporators and, constitute a major BOD source. There is a discrete condensate stream from each of the several evaporator bodies, but the BOD distribution is very uneven, and it is normal practice in the more modern mills to segregate the condensate streams to facilitate reuse. All the condensate is hot and the less contaminated streams are suitable for use in the recausticising and pulp washing departments.

The condensates are also contaminated with small quantities of black liquor which are carried over in the vapor heads of the evaporators. The designer's objective is to minimise this carryover, and in well designed, adequately sized units it is usually negligible. However, multiple effect evaporators are not easy to operate, particularly if they are overloaded or poorly instrumented, and liquor carryover is a frequent problem. Several kg BOD/tonne pulp can be transferred to the condensates by this carryover, and will pass through any condensate stripping system. More seriously, carryover can cause foam generation in a condensate stripper, and prevent its operation so that both the volatile BOD from the true condensates and the BOD of the black liquor which is carried over will be added to the mill effluent.

Since the environmental aspects of evaporator condensates became important in the 1970's, considerable development has taken place in design of systems, and a modern evaporator running at its design capacity can operate with only a few percent of the carryover of black liquor of older or overloaded systems. Current evaporator design criteria require a maximum of 1 gram sodium carryover / tonne condensate

3.4.3 Condensate Properties

The contaminated condensates contain 8 -15 kg BOD/t pulp. The BOD is caused by alcohols, ketones, terpenes, phenolics, resin and fatty acids, and the total reduced sulphur (TRS) compounds. Methanol is the most significant factor in the BOD load. Most of the organic material is low molecular weight material which is readily converted to water, carbon dioxide and other harmless compounds in a biological treatment system of the receiving waters, if there is sufficient oxygen available.

Reported 96-hour LC50s for contaminated condensates range from 0.04% to 17%, using fish. Many of the contaminated condensate's components, such as the TRS compounds, and resin and fatty acids, are lethal at concentrations well below their concentration in contaminated condensates. The TRS compounds appear to be the dominant factor in contaminated condensate toxicity.

Some workers have suggested that the role of TRS compounds in the toxicity of kraft mill effluent is minor, on the supposition that the compounds should be rapidly oxidised or air-stripped in the mill sewer system and in the receiving waters. However many others have concluded that these condensates contribute 20 - 50% of kraft mill effluent toxicity. The wide variation in reported data is at least partly due to the difficulty of separating true condensate from black liquor carryover.

Contaminated condensates have been found to taint fish flesh at concentrations in water between 0.1% and 2% and may contribute 20% of tainting properties of a bleached kraft mill (Cook et al 1973, Blackwell et al. 1979) The compounds responsible for the tainting are not definitely known, but phenolics and the TRS compounds are likely major contributors.

Measured odour detection thresholds of contaminated condensates in water range from 0.5 - 60 ppm. Taste thresholds of contaminated condensates in water range between 50 - 200 ppm. TRS compounds are generally considered to be the main source of water odour and taste. The detection threshold usually represents judgement by a human test panel since concentration are at the practical lower limits of analytical or instrument technology.

Contaminated condensates contain about 0.3 kg TRS (as S) per tonne pulp. Since some of the TRS compounds in the condensates are stripped from aerated lagoons by the process of aeration, sewered contaminated condensates can represent a significant source of odour at a biological treatment system. Contaminated condensates represent several percent of the total mill effluent volume so they can be considered high-strength low-volume wastes that are logical candidates for selective waste treatment.

3.4.4 Condensate Stripping

The contaminated condensates from the multiple effect evaporators and digesters are frequently steam stripped to remove TRS and BOD as shown in Figure 3.2. Some mills have used air stripping or waste gas stripping to energy consumption . Some of the older steam stripping systems required one tonne steam per tonne of pulp for effective operation, which represents about 15% increase in purchased energy costs for a typical bleached kraft mill. The recent developments in steam stripping have concentrated on reducing the energy consumption of this process, since many of the systems installed in the 1970's have proven to be excessively expensive to operate at their design efficiency.

Improved segregation of condensates has reduced the volumes which must be stripped to as low as 1.8 m^3/t pulp in mills with continuous digesters. This has been achieved by the installation of segregated two-stage surface condensers and very detailed engineering analysis of the remainder of the digester and evaporator design features which contribute to the production of contaminated condensates.

Systems have been installed which take advantage of the fact that in most mills the lowest pressure steam header is at a pressure of about 300 kPa, whereas the evaporator requires steam at about 200 kPa, so the stripper is inserted in the evaporator steam supply line. This can reduce the steam requirement for stripping to a fraction of a tonne steam per tonne pulp.

The theoretical heating value of the gases produced by a steam stripper corresponds to about half a gigajoule per tonne pulp, so it is potentially feasible to develop a condensate stripping system which recovers more energy than it consumes. This performance has been claimed for some systems but commercial scale evidence is not yet available.

Instead of attempting to reduce steam consumption, several installations have adopted the approach of air stripping the contaminated condensates to reduce the TRS content and then allowing the waste heat in the smelt dissolving tank or the lime kiln scrubber to strip the methanol out and discharge it to atmosphere. No mills have taken maximum advantage of the possibilities of this approach to date, and many of the mills are unaware that BOD is being stripped in this manner. Current stripping technology was summarised by

Burgess (1987). Beak (1982) discusses the use of waste gases for stripping contaminated condensates and also includes extensive data on the established stripping techniques.

Despite the proven capability of condensate strippers to reduce effluent BOD and toxicity, a stripper is often very inefficient economically as an environmental protection measure. The first reason is that most of the "low molecular weight" compounds which are removed can be removed biologically at much lower cost, if the mill has a biological treatment system, and in cases where the receiving water volume is sufficient to avoid short term oxygen deficiencies, natural degradation of the low molecular weight compounds is efficient and is adequate to protect the environment. Although a suitably designed steam stripper can remove at least 10 kg BOD/t pulp from the mill effluent, it will consume about 0.5 t steam/t pulp. At typical steam costs this is equivalent to around $3.50/t pulp, in addition to the associated capital and maintenance costs.

3.4.5 Soap Recovery

Soap skimming has long been a part of the kraft process but in recent years has become more important. A major reason for this is that resin acids contained in the soaps are one of the major toxic components in pulping effluents and also have an adverse effect on biological waste treatment systems. Soap skimmings consist largely of resin acids and fatty acids present in the original wood which on pulping become saponified in the alkaline liquor, forming their sodium salts. In the dilute spent cooking liquor these salts remain soluble, but during evaporation their solubility decreases to the point where they begin to "salt out". This usually occurs at a black liquor solids concentration of 25 to 35%. This material is termed soap and can be removed by a rotating paddle at the surface of the liquor in a skimming tank. Where maximum soap removal is desired, the skimmer is normally located part way along the evaporator chain, where the black liquor concentration is around 30%.

Approximately 80 kg soap is formed per tonne of kraft pulp, typically containing 40% resin acids and 30% fatty acids. The BOD of soap approaches 100,000 mg/l, and its **LC50 for fish has been measured as 6 mg/L, i.e. very toxic**., so it is obvious that soap will have a significant effect on effluent quality if it is discharged to the sewer. The toxicity of resin and fatty acids is further discussed in Section 8.

An adequate retention time in the tank (1.5 to 2.5 hours) permits the soap to float to the top. The skimmed soap may be converted to tall oil on-site or sold to an external tall-oil plant. Alternatively it can be burned in the recovery furnace, effectively destroying it and recovering the heat and chemical value.

Since the soap can represent up to 10% of the total heat load on the recovery boiler, there is an opportunity to reduce the load on the latter by burning the soap elsewhere. It is fairly common practice to ship soap to other mills for incineration. Recently some mills have investigated burning the soap in the hog fuel boiler, although there is no published literature on actual operations. McCubbin (1983) concluded that it is theoretically practical and economically attractive to incinerate the soap in the mill's lime kiln, but that there was no experience of such practice.

If there is no soap skimming equipment installed, there is a tendency for layers of soap to form on top of the strong black liquor storage tanks where some of this overflows to the sewer. Some mills with lower soap content liquor can effectively control soap losses simply by intermittently pumping off this layer and incinerating it. If there are no specific measures taken to avoid soap discharge to the sewer, then it will raise the toxicity of the mill effluent. A spill can be disastrous, and in one case there was a twenty-minute overflow which caused fish mortality over 45 km of river.

3.4.6 White Liquor Production

The molten smelt which flows from the smelt bed in a recovery furnace is composed mainly of sodium carbonate and sodium sulphide. This smelt drops through steam shatter sprays into a dissolving tank where it is dissolved to form green liquor, which is then causticised by mixing lime and water in a slaker. The reaction in the slaker takes place at around 100°C.

The mixture of calcium carbonate, sodium sulphide, sodium hydroxide and water produced by the causticiser is routed to the white liquor clarifier where the calcium carbonate settles out. The clarifier product is white liquor, which is the principal chemical ingredient in the cooking liquor required in kraft pulping as described in Section 3.1.2

The settled mud is washed by dilution then rethickening in another clarifier known as the lime mud washer, and then thickened to about 70% consistency in a vacuum filter and re-calcined to quick lime, CaO, in the lime kiln. A few mills use fluidised bed calciners instead of lime kilns.

Virtually all mills which have oxygen delignification systems use a portion of the white liquor to supply the necessary alkali required in the oxygen reactor. White liquor contains about 25% sodium sulphide (NA_2S), and the latter must be oxidised by contact with air or elemental oxygen, as shown in Figure 3.6

3.4.7 Recovery Cycle Effluents

Theoretically, the only effluents from the kraft recovery areas would be evaporator condensates, green liquor dregs, and slaker grits as discussed above. However, there are a number of intermittent discharges due to spills of black liquor which can be up to 20 kg/BOD per tonne pulp. Good design and operating practices will reduce these spills to a few kg/t, and a spill control system, as discussed in Section 3.8, is necessary to achieve a high level of environmental protection.

3.5 Recovery Boiler Capacity

SUMMARY The capacity of the mill's recovery boiler is often a limiting factor in attaining a high level of environmental protection. It is always technically feasible to reduce pulp production to release whatever recovery boiler capacity is required for environmental protection purposes, but this imposes an economic penalty. Replacement of an existing boiler would be expensive for many mills, but there are a number of potential technical solutions which are discussed in this section.

Oxygen delignification, extended cooking, PRENOX and improved brownstock washing/screening can produce up to 12% additional black liquor solids in a mill which currently has relatively high losses of black liquor solids to the sewer. Where the mill already has good washing (soda losses under 10 kg Na_2SO_4/t pulp), the additional recovery boiler load would be about half the above value. Refer to the sections of the report discussing these process modifications.

The operation and design of the recovery boiler are very important in the regulation of atmospheric emissions, and adequate recovery boiler capacity is essential if water pollution is to be minimised. Historically, recovery boilers have been rather undersized relative to the production capacity of the other processes in most North American mills, so it is common for the recovery boiler to be a key bottleneck in mill production.

Ideally, all organic material removed from the wood in the process of producing bleached kraft pulp would be incinerated in the recovery boiler. This is impractical in the case of organic material containing chlorine, since the chlorides produced will accumulate in the recovery cycle, causing severe corrosion and eventually preventing its operation.

Modern practice is to design the recovery boiler to burn all the organic material and recovered chemicals produced from the cooking and brownstock washing processes in the mill. Where delignification is extended by oxygen bleaching, special cooking procedures or other techniques, an additional quantity of organic material is produced, which should be burned for environmental reasons, but which may create capacity limitations, so the issue of the capacity of the recovery system to process all the black liquor produced is critical in a mill attempting to minimise the discharge of aqueous pollutants.

3.5.1 Defining Capacity

There is no universally accepted definition for Recovery Boiler Capacity. For this report it is defined as the **maximum quantity of black liquor solids that the boiler can burn, safely, reliably and without emission of excessive quantities of Total Reduced Sulphur (TRS) gases**. The latter cause the traditional disagreeable kraft mill odour. Boiler capacity is normally specified by the boiler manufacturer in terms of the feed of liquor solids per day, and this value is calculated by considering a number of aspects, including the heat release rate in the furnace, gas flows, rate of steam generation and the capability to reduce sodium sulphate in the feed liquor to sodium sulphide. Chamberlain (1981) discusses practical recovery boiler capacities.

In evaluating the capacity of recovery boilers, it should be noted that most boiler operators consider their boiler to be overloaded, since they have to work hard to make it run reliably. A detailed technical study is required to assess the real capacity of any recovery boiler. In most cases, the key parameter is the total calorific value of the black liquor solids fed to the boiler, since this in turn determines the quantity of air required to achieve satisfactory combustion, which in turn determines the flue gas flow. This is significant in the context of this report, since there are several ways of reducing the calorific value of the liquor fed to the boiler, which can be used in practice to solve the problem of increased the production of black liquor solids which accompanies the introduction of processes to improve effluent quality.

Personnel safety is an especially important issue with respect to recovery boilers. Experience has demonstrated that kraft mill recovery boilers are much more likely to explode than most other boilers, and many have done so, frequently with fatal consequences. Recovery boiler technology, including the safety aspects, has improved steadily over the past twenty years. **Any modifications to recovery boilers to increase their capacity to burn black liquor must be designed to maintain a high level of safety for the operating personnel.** Some potential modifications intended to increase recovery boiler capacity, such as increasing the consistency of the feed liquor, inherently enhance safety.

3.5.2 Upgrading Existing Boilers

In practice, the recovery boiler itself is usually the most critical element in the chemical recovery system. Management of a mill who wish to modify the production process to improve effluent quality by recovering and incinerating organic material can be faced with installing a new recovery boiler. Technically, this is always feasible, since the technology is well proven and developed, but the capital cost is generally in the 50-100 million dollar range, so that economic constraints are significant, and alternatives have to be considered, including reducing the load on the boiler.

It is generally considered to be impractical to increase the boiler capacity marginally, but several mills have done so. A current Canadian example is the recently announced project at Cariboo Pulp and Paper in Quesnel, BC.

3.5.3 Reducing Boiler Load

SUMMARY It is often more practical to reduce the load on the recovery boiler than to increase the capacity of an existing installation. It is necessary to analyse the mass and energy balance of both the boiler and the complete kraft chemical shown in Figure 3.1, with careful consideration of the capacity of each piece of equipment in the system, to determine which of the available techniques are technically and economically feasible. The items discussed below show that there are a number of ways of obtaining several percent additional capacity form many boilers, but the list is not exhaustive since there is extensive scope for engineering ingenuity in this field.

The simplest way of reducing load on the recovery boiler is of course to reduce the production of pulp. The economic cost of decreasing production will generally, however, be large and will be the least attractive option available to the mill. Most mills already practice some of these techniques, but no mills practice all of them, so the attainable reduction in boiler load will vary from mill to mill.

If the **soap is separated** and sold, burned outside the recovery boiler or converted to tall oil, the heating value of the black liquor is dropped by 4% to 8%. Hardwoods would be at the low end of the scale, and softwoods the top. Several Ontario mills already practice soap separation so the scope for using this technique for further reduction in boiler load is limited.

Oxidising the black liquor, using well proven processes, will reduce the heating value of the liquor by 2%.

Where a mill has inadequate storage for black liquor and other recovery cycle streams, the boiler never operates optimally, and can lose several percent of its capacity. At least one mill known to the authors has added 5% to its effective recovery boiler capacity by **increasing black liquor storage capacity** from 3 hours retention to 24 hours retention, which allowed the operators to adjust the boiler for optimum operation. This major improvement in capacity was of course possible only because previous operation was poor. The effect of increased black liquor storage on effective boiler capacity is very mill-specific.

A number of mills in North America and Europe **transport black liquor to other mills for incineration**, sometimes buying back the white liquor produced. This is a practical solution to overloaded recovery boilers if there is a mill with spare capacity within about 200 miles.

As mentioned in Section 3.2.2, addition of **anthraquinone** to the digester has been proven to improve the pulping yield by up to 2.5%, which reduces the production of black liquor solids by up to 11%. Yield increases of 1% with **boiler load reductions of about 6%** are typical of mill operating practice.

At least one Ontario mill uses anthraquinone, and over 60% of Japanese mills and many others in the world do so. The operating cost of compensating for various increases in recovery boiler loads caused by the introduction of oxygen delignification is shown in Table 3.3. . The capital cost is negligible.

High-consistency liquor firing is gaining acceptance (Hyoty and Ojala 1968). This involves installing an additional black liquor evaporator, sometimes known as a "super concentrator" to raise the consistency to around 80% dry solids. Such liquor is more difficult to handle than the traditional thick black liquor at around 70% consistency, but when burned it generates less gas flow in the recovery boiler due to its lower water content. Since boiler gas flow is one of the key factors limiting capacity, it is possible to increase effective recovery boiler capacity by more than the 5% required to accommodate the additional solids in the black liquor.

Where steaming rate is the limiting factor on recovery boiler capacity, some improvement can be attained by **reducing the boiler feed water temperature and/or reducing the temperature of the combustion air** where it is heated by the steam coil air heated. Either of these techniques reduce the steaming rate by several percent.

Where **gas flow** is the limiting factor in boiler capacity, it is possible to compensate to the extent of at least 10% of boiler load by enriching the combustion air with oxygen. The boiler at the MoDo mill in Husum, Sweden has reportedly (Croon 1983) operated for a one week trial at 17% greater load with oxygen enrichment than without, but the cost was excessive.

3.5.4 Recovery Boiler Replacement

The foregoing measures demonstrate that there are many practical alternatives to replacing a recovery boiler when pulp production, installation of oxygen delignification or other change in mill operation results in a recovery boiler being overloaded. Some are primarily "stop-gap" techniques which allow a mill to maintain pulp production for a few months or years without having to incur the high capital cost of a new recovery boiler, while others are good investments in themselves.

However, a new, modern boiler offers a number of advantages, which serve to partially offset its cost. These include greater thermal efficiency, reduction of air pollution, reduced labour, and greater pulp production capacity. Recovery boilers generally have a useful operating life of about twenty years, so it is common for mills to install new boilers for non-environmental reasons from time to time.

3.6 Papermaking

The bleached kraft pulp produced in Ontario kraft mills is either dried and shipped to off-site paper mills, or stored in slush pulp form and pumped to on-site paper mills. The latter arrangement is generally known as an integrated mill.

The mills at Marathon, Smooth Rock Falls and Terrace Bay are non-integrated and all their product is shipped elsewhere for use as raw material in paper mills. The mills at Red Rock and Cornwall use all kraft

pulp produced on-site, while the mills at Fort Frances, Thunder Bay, Dryden, and Espanola use some pulp on site, and ship the rest to paper mills.

The papermaking operation is a relatively small contributor to mill effluent in Ontario kraft mills, due to the nature of the operations and the fact that only a portion of the bleached kraft produced is used on site. Cornwall is an exception, since it is effectively a large paper mill, with a relatively small pulp mill on-site. Red Rock is also an exception since very little of the kraft pulp produced is bleached.

The papermaking processes are described in many texts. McCubbin (1983) describes the papermaking with an emphasis on environmental aspects.

Stock generally arrives in the paper machine area at a consistency of between 3 and 12%. The final product is about 90% dry, so that from about 7 to 30 tonnes of water must be discharged per tonne paper produced. In addition, up to about 15 tonnes water per tonne paper are added by the paper machine showers and pump and agitator seal water, which must also be discharged at some point.

Cleaner and screen rejects can be up to a few percent of total production but are normally under 1%. It is not possible to define an "acceptable" rate of suspended solids discharge since it depends on the product specifications, and cleanliness of the pulp furnish.

In most cases it is feasible to dewater the rejects and landfill them instead of discharging them to the sewer. However, if the mill has a primary effluent clarifier with adequate sludge handling equipment, it may be more economical to discharge these rejects to the sewer so that they will be recovered in the clarifier. If the ash content of the rejects is low, they can be burned in a bark boiler. However a low ash content generally implies a high fibre content, and suggests that the better way of reducing the suspended solids discharge would be to improve the cleaning system so that it can provide acceptable quality stock with a reject low in fibre.

About 1.5 tonnes of water per tonne of paper is evaporated, and a large proportion of the remaining water is used for stock dilution prior to the paper machine area of for washing in beach plants. However, there is usually excess white water to be discharged to the sewer, which inevitably contains suspended solids in the form of fine fibres and in some cases fillers. If the mill has a modern disc saveall properly integrated with the white water system, only clear saveall filtrate will be discharged to the sewer, except during shutdowns or grade changes. For most mills the suspended solids concentration of this stream would be under 150 mg/L, and the mass flow of suspended solids would be under 3 kg/t paper, perhaps almost zero. If the mill produces filled or coated paper, these discharges could be much higher. Frequent grade changes also tend to cause relatively high suspended solids discharges with the white water. Unfortunately, it is a characteristic of the paper market that the filled papers are produced in relatively small batches, requiring frequent grade changes, and such factors have a major impact of the overall mill effluent in mills such as Domtar at Cornwall.

The source of BOD of paper mill effluents are dissolved wood organics, fine fibre particles and coating material. Generally none of the dissolved wood organics reach the paper machine in the case of bleached chemical pulps, but much of the kraft mill organic loss appears in the paper machine sewer in a mill like the one at Red Rock.

Coating and filler materials include starches, latex and other organics. Some leak to the sewer and about , 20% of the total used in the mill is introduced to the white water by way of the broke system. Most of this is discharged to the sewer. The quantities vary widely, but 10 kg BOD/t paper is not unusual.

In general, the chemical concentration of additives used in the stock system is sufficiently low as to have no toxic effect on fish. However, at high concentration, some of the additives may be quite toxic. The use of some persistent toxic chemicals such as mercury compounds to control bacterial growth in the paper machine white water system was discontinued in Canada in the early 1970's.

There is no doubt that a proportion of the dioxins and other organochlorines, which pass from most kraft mills into the paper mills along with the fibre, leach out in the paper mill effluent. There is a paucity of data in the literature, but this will be rectified in 1988 in view of the extensive interest in dioxins, the MISA program, and the demands by some European pulp customers for data on organochlorines in the pulp.

3.7 In-plant Effluent Reduction Processes

SUMMARY The term "in-plant" is used to refer to measures to reduce aqueous emissions from mills by modifications to the production process, in contrast to treating the effluent by external treatment systems. The concept behind all in-plant water pollution control measures is that much of the effluent from a mill is caused by losses of chemicals or fibre which can be reused in the process or incinerated in the lime kilns or boilers in the pulp mill. In most cases, this requires the installation of additional equipment, but some measures are simply improvements in operating practices, or improved operator training. An essential advantage of most in-plant effluent reduction processes is that they do not generate sludges or other waste streams to be disposed of. An essential disadvantage is that they are more complex than external effluent treatment systems, which can create difficulties for regulatory authorities who must approve systems and monitor performance. Even the best external effluent treatment system requires in-plant spill control if it is to be reliable.

3.7.1 Concept and Principle

Many of the potentially useful in-plant process modifications are discussed in the foregoing sections. Some additional aspects of in-plant effluent reduction are discussed below

3.7.2 Oxygen and Chlorine Dioxide for Reduction of AOX

The individual technologies and environmental effects of oxygen delignification were discussed in Section 3.3.12, and substitution of chlorine dioxide for chlorine in the chlorination stage of the bleach plant was discussed in Section 3.3.10. Both technologies can be used simultaneously.

Oxygen delignification has been in commercial use for 18 years, although it is only now becoming widely known among environmentalists in Canada. It has been used successfully since the late 1970's by the E.B. Eddy mill at Espanola.

High substitution of chlorine dioxide has been in operation for ten years or more, and is used increasingly around the world, but seems to have escaped the environmentalists notice. Pryke mentioned in his presentation to the CPPA Annual Meeting (1988) that 4.5 million tonnes pulp per year are bleached using high substitution, and that this would increase by almost 50% during 1988, presuming that all mill modifications currently announced are completed on schedule.

Norström (1987) states that oxygen delignification is the obvious and most efficient first step, if one wishes to reduce the discharge of organochlorines, and Swedish literature in general follows this philosophy. The present authors agree that this is probably true for a new mill, or one where there is an unusually good opportunity to install the oxygen delignification systems at low cost because it will eliminate the need for some other major investment in the bleach plant.

However, in the case of existing mills, there are a number of advantages in considering high substitution of chlorine dioxide, as the logical first step, since it can reduce organochlorine discharges by up to 60%, depending on the current substitution level. The principal advantage is that substituting chlorine dioxide for oxygen does not increase the load on the recovery boiler, which is critical in some mills, although of minor importance in others.

The effects of these two process modifications are additive, as shown in Figure 3.11. This is based on a typical softwood kraft mill, and shows the effect of substituting various amounts of chlorine dioxide for chlorine in the chlorination stage. The curve for oxygen delignification shown assumes that 45% of the lignin in the washed brownstock would be removed by the oxygen stage

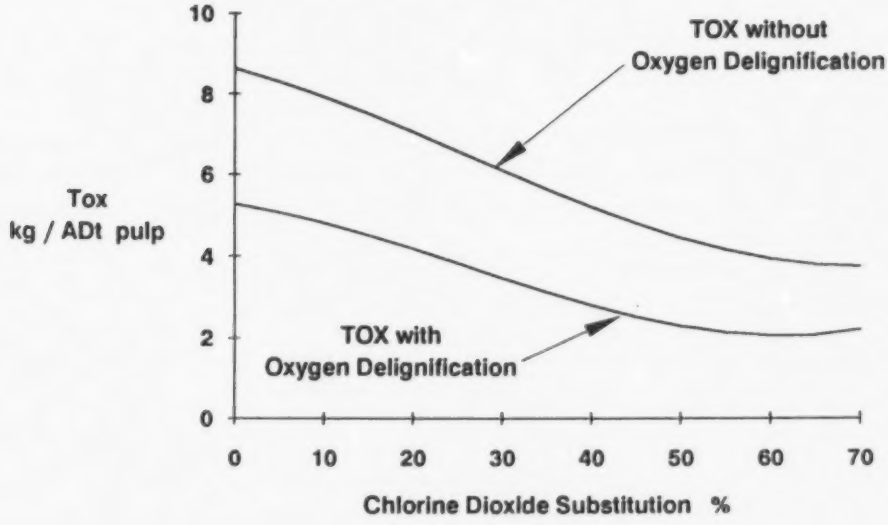

Figure 3.11 Comparison of effects of oxygen delignification and chlorine dioxide substitution on organochlorine discharges. Calculation by authors based on Germgård (1983) and du Manoir (1982)

The indications of reduced toxicity discussed in Section 3.3 are welcome, but the major advantages of oxygen delignification and substitution of chlorine dioxide for chlorine are still the reduced usage of chlorine, with consequent reduction of persistent chlorinated toxicants, some of which may not show up to any extent in the acute toxicity tests.

3.7.3 Chlorine Free Bleach Sequences

SUMMARY Kraft pulp has been bleached in laboratories to market quality without using any chlorine or chlorine compounds in the process, but there have not been any full scale installations.

Clearly, if there are no chlorine compounds entering the bleach plant, there will be no organochlorines leaving, whether chlorinated dioxins or others.

A number of researchers studied chlorine free bleaching processes in the late 1970's and early 1980's, and several concluded that market hardwood kraft could be bleached without chlorine, including Schleinkofer (1985). Eastern Canadian softwood kraft was bleached to market quality in the laboratory (Liebergott et al. 1987)

A bleaching sequence (OZEPY) using oxygen followed by ozone and caustic extraction to delignify the pulp, then hydrogen peroxide and sodium hydrosulphite to brighten it to 90.1 ISO brightness was evaluated in the laboratory . The pulp opacity, bulk, burst, tear, breaking length, stretch and MIT folding tests were virtually identical for the OZEPY bleached pulp and for a control pulp which was bleached by a traditional CdEDED sequence. These data were determined for samples at both 300 and 500 Canadian Standard Freeness, and the beating energy was 35% lower for the OZEPY pulp than for the control pulp. Not surprisingly, the viscosity was about 25% lower for the OZEPY pulp, but we consider that this is unimportant, as discussed in Section 3.3.1.

Liebergott presented an economic analysis which showed that there was little or no difference between the capital and operating costs of the traditional and OZEPY bleaching processes. Our own brief analysis of his process data indicated that there would be some significant economical advantages for the OZEPY process at current Ontario chemical costs, if the regulatory framework recommended in this report is adopted. **However, it would be necessary to build an industrial scale pilot plant and operate it for at least a year to gain sufficient knowledge to evaluate the technical and economic feasibility of this process, so it cannot be considered as proven technology at present.**

There are signs of renewed research activity, which is appropriate in view of the current interest in organochlorines. The current costs of the principal chemicals, ozone and hydrogen peroxide, are lower in 1988 than they were at the beginning of the decade when the non-chlorine bleaching research was most active. We recommend that the Ministry encourage such research.

3.7.4 Peroxide

Hydrogen peroxide can be used to extend the delignification of an oxidative extraction stage in a conventional bleach plant, thus reducing the input of chlorine in subsequent stages. This reduces the organochlorine discharge, by a few percent in addition to the benefit mentioned in 3.3.11 above concerning Alkali/oxygen extraction.

Hydrogen peroxide can also be used in bleaching sequences aimed at eliminating chlorine, and toxicity of the wastewater is similar to or somewhat less than toxicity from conventional chlorine bleaching. There are other advantages of course, since in some cases the peroxide and acid pretreatment stages could be recycled back to the recovery system, achieving reductions of 90% in colour, 40% in BOD, and finally, no chlorinated organic substances (Dugal and Ruhanen 1981).

The relatively high cost of hydrogen peroxide has been a major impediment to its use in the past, but prices have dropped relative to other bleaching chemicals.

3.7.5 Rapson process

The Rapson process (Great Lakes FP 1980 and McCubbin 1984) appears to offer the possibility of a zero effluent mill. It is based on extensive recycling of the bleach plant process water, and the use of all bleach plant effluent for brownstock washing, so that all organic matter removed from the pulp during bleaching would be incinerated in the recovery boiler. This could eliminate the discharge of organochlorines, including dioxins, but there is no data available on the quantities of dioxins in the recovery boiler stack gases, if any.

It is now clear that it will be impracticable to operate a mill on a completely closed cycle, due to the build-up of metals in the process, but the possibility of destroying a high proportion of bleach plant organic wastes by incineration has some obvious environmental advantages.

A full scale system was installed in the Thunder Bay mill in the 1970's, but had to be abandoned after several years due to a variety of reasons including corrosion. We do not consider the Rapson process to be proven technology.

3.7.6 Control of Chloroform Formation

Chloroform is produced when kraft pulp is bleached, and bleach plants which use sodium or calcium hypochlorite ("hypo") produce in the order of 10 times as much chloroform as those which do not use hypo. (Crawford et al 1987).

Up to 20% of the chloroform produced in bleacheries using hypo is formed in the chlorination stage (Crawford), particularly where an unusually large amount of chlorine is used relative to the Kappa number of the incoming pulp , in order to compensate for inadequate equipment. Some of this chloroform is discharged with the caustic extraction ("E stage") filtrate. (Refer to Figure 3.2).

Hypo bleaching stages were installed immediately downstream of the first E stage [7] in many pre 1970 bleach plants, but have rarely been installed in recent years.

Crawford summarised the technology available for control of chloroform formation. Reduction, or elimination, of hypo usage is the principal approach. In many mills this would require the installation of an additional chlorine dioxide stage (tower, washer and auxiliaries) and conversion of the former hypo stage to a second E stage. Where the mill uses the CEHDED bleaching sequence, it is normally possible to simply abandon the hypo stage and adjust the chemical dosages. The introduction of alkali-oxygen extraction discussed in Section 3.3.11 has created opportunities to produce high quality pulp without hypo.

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[7] Figure 3.2 does not show a hypo stage

3.8 Control of Accidental Losses

SUMMARY (1) The control of accidental losses is an essential part of the water pollution control strategy of any mill aiming at a high level of environmental protection. (2) As the average discharges from mills decrease, the relative importance of accidental losses rises, and in many mills it is more environmentally beneficial to take steps to reduce accidental losses than to reduce the normal day-to-day discharges. (3) The soap which collects in black liquor tanks is the most significant of several process fluids that can cause serious spills if adequate control measures are not implemented. (4) Personnel training and competence are the most important factors in any spill control plan.

3.8.1 Sources

Accidental losses are defined as discharges to the environment caused by abnormal operating conditions, and which are in excess of the discharges which occur when the process is operating normally. They are usually caused by equipment malfunctions or human error (including errors by the mill designer who failed to foresee a particular set of operating conditions).

Very little solid data are available on the extent of accidental losses, partly due to operators' natural reluctance to advertise their mistakes, and also due to the difficulty of measuring the actual quantities. In some mills with very tightly closed process cycles and low normal losses, the accidental losses can be as much as 60% of the monthly averages. A range of about 20 - 30% is probably typical except for mills with very high continuous discharges. In some cases these accidental losses can be spectacular and can cause environmental damage or extreme public reaction.

Large and deadly spills have been rare in kraft mills in recent years, but their importance scarcely needs documentation here. We need only think of the massive fish kill in 1983 along 45 km of the Spanish River. The mill involved has had a splendid record of meeting toxicity regulations in recent years, and had already installed oxygen delignification at the time of the accident, but a 20-minute spill from a tank of resin and fatty acid soaps was enough to kill the fish.

Accidents can be made rare, but they will always be with us. The real problem, in dealing with toxic spills at pulp mills, is that they may go undetected for some time, since toxicity cannot be monitored continuously and there is no alarm bell to warn of an increase. Thus the waste may reach the receiving water before anyone is aware of a problem. Fortunately, sodium salts are also contained in most spills of toxic material in the kraft pulp industry, so that conductivity monitoring instruments can be used to warn of toxic spills within a few minutes of the spill commencing. To be effective, these conductivity monitors must be strategically placed, and operators must be trained to recognise the significance of alarms, and how to react to them.

It is convenient to divide accidental losses into two classes, spills and dumps. Spills consist of overflows, leaks etc which occur more or less instantaneously.

Dumps are discharges of effluent which are deliberately caused by operator action. These often occur in circumstances where the operator has no other choice. For example, if the suction valve of a pump is jammed by a wooden plank, it may be impossible to pump the tank out to gain access to clear the blockage, and there is no alternative but dump the tank to the sewer in many mills. The solution is to design or modify the mill so that the operator has a realistic alternative, but this must be done before the

emergency occurs. Dumps can also be caused by lack of operator knowledge or environmental concern, and by failure to plan maintenance shutdowns so that the levels in tanks which must be entered are low.

3.8.2 Design for Control of Accidental Losses

The first step in controlling accidental losses is to design and build the plant in accordance with good engineering practices. Equipment which is mis-applied fails relatively frequently, often causing accidental losses to the sewer. At the design stage, it is essential to evaluate the effects of all the likely modes of equipment failure on the overall mill process, since failure in one department is frequently the cause of spills in others. There is extensive experience available on the failure rates of all the conventional equipment but risk analyses on the overall system are rarely included in mill design, due to the time required. Process simulation software is available to facilitate computer modelling of mill operations, which allows the mill designer to make effective use of the available knowledge on individual equipment failures and incorporate suitable spill control features in the mill design, but it is rarely used in the pulp industry for this purpose.

Adequate intermediate storage for process chemicals and partially manufactured product (as discussed in Section 3.8.3) is important if accidental losses are to be minimised.

Good design and adequate storage facilities are usually sufficient to control accidental discharges to the sewer in many mills which have generously sized waste treatment systems. However mills which wish to comply with regulations without external effluent treatment or who have marginally sized treatment systems, require to install sophisticated spill recovery facilities in the higher risk areas of the mill.

The frequency of occurrence of accidental losses can be reduced, but not eliminated, by the intelligent interconnection of tanks, installation of standby pumps and the provision of spill sumps as described later in this section.

Demands for improved working conditions in the 1960's led to the practice of installing generously sized floor drains for all potential overflow points. Unfortunately this made spills less visible to operators and supervisors, and thus removed one disincentive to sloppy operating practices. Recently several companies have adopted the policy that the mill layout should make spills visible and even sometimes inconvenient by installing floor drains for continuous effluent streams only. This is generally desirable, provided that the inconvenience does not extend to representing a health hazard or risk damaging equipment. Complex floor drainage systems are expensive, so this approach can reduce capital costs.

Substantial reductions in effluent discharges can often be achieved by installing collection sumps at key points in the mill to recover overflows and leaks from tanks and equipment. In some cases these can be effectively implemented by segregating certain of the floor trenches, which exist in most process areas, and routing them to the spill collection sump. However, in most cases contamination of the recovered material or excessive dilution by clean water prevents such a simple solution, and special piping must be installed. The weakest aspect in the design of many systems for control of accidental losses is that they collect too much water and lightly contaminated effluent, so that the material "recovered" is too dilute to be recycled.

The material collected in the spill sump must be returned to the process system, either directly or it may be stored in a spill collection tank pending analysis and a decision made on the best time and location for its re-use. In some cases, it is most appropriate to discharge the collected spill slowly to the sewer.

Generally, the majority of spills and dumps occur in a few relatively restricted areas of the mill, and it is normally in these key areas that accidental loss recovery systems can be effective. Table 3.9 lists the areas where such recovery systems are usually necessary, together with the most popular points of re-introduction to the process. **The soap which collects on the surface of black liquor storage tanks is the single most toxic substance found in kraft mills** when due account is taken of the quantities involved as well as its high toxicity. It is essential that effective means of preventing soap spills are provided in any mill aiming at a high level of environmental protection. A soap spill was the prime cause of the widely publicised fish kill on the Spanish river a few years ago.

Many mills recover soap and convert it to tall oil for sale. While this is environmentally desirable, it does increase the risk of a spill since the toxic material must be stored and processed, so appropriate precautions are necessary to avoid spills of soap and tall oil.

Table 3.9 Typical accidental loss recovery systems.

Mill area	Type of loss	Process re-entry point
Digester	Unwashed stock	Blow tank
Screens	Washed stock	Screens
Evaporators	Soap	storage and/or incineration
Evaporators	Black Liquor	Weak Black liquor storage
Recovery Dept.	Black liquor	Weak black liquor storage
Bleach Plant	Partly bleached stock	Ahead of bleach plant
Chlorine Dioxide Plant	Sulphuric acid	Dilute and neutralise

The design of accidental loss prevention and recovery systems is site specific, particularly with respect to the selection of the locations for re-introduction of the recovered material to the process.

3.8.3 Intermediate Product Storage

Ideally, a pulp or paper mill would operate continuously, with the rate of production in all departments adjusted to match each other's needs. However this is impractical due to unforeseeable equipment problems as well as the need to shut down certain departments (typically for an 8 hour shift) for periodic maintenance. Some storage is therefore required between each major department, and the adequacy of this storage has an impact on accidental losses. Mills generally discharge the least effluent when they are operating without upsets, and adequate storage between the major production units assists in stabilising operations

In principle, mills with generously sized effluent treatment facilities can comply with effluent quality regulations, even if storage capacities are inadequate. However, there are practical and economic constraints on the size of spill that can be effectively treated by a waste treatment system. A technical and

economic compromise between storage, accidental loss prevention and effluent treatment facilities is necessary in all mills.

In all cases, those mills where very tightly closed process cycles are utilised to reduce effluent discharges, storage capacity must be sufficient for mill staff to diagnose problems and take the appropriate corrective action prior to any major spill occurring. This generally requires storage capacities of around the higher values mentioned below.

There is no absolute mathematical method for selection of the size and location of intermediate process storage tanks, but the following represent good practice in kraft mills:

12 to 24 hours capacity of washed, unbleached pulp, usually at "high-density" (about 12% consistency);

12 to 24 hours each capacity for weak black liquor and strong black liquor;

24 hours capacity for white liquor (some of this may be in the white liquor clarifier);

12 hours capacity for weak-wash (some of this may be in the lime mud washer); and

8 to 24 hours storage for bleached stock, normally at high-density. The storage capacity is generally highest when a complex installation such as a paper mill follows the bleach plant rather than the relatively simple pulp dryer.

3.8.4 Operating Practices and Housekeeping

Much of the action required to control accidental losses can be described as good housekeeping or "running a tight ship", since many dumps and spills are due to simple errors which are relatively easily avoided. The most advanced technology and exotic equipment is ineffective if it is poorly operated or maintained.

Operating practices and training have an important impact on all aspects of mill operations, but particular attention is required to the control of accidental losses. Historically, much of the operator training in the pulp and paper industry has been based on the operating manuals provided by the suppliers of the equipment. While this can be effective in attaining production levels and meeting product quality specifications, it is less satisfactory with respect to the control of accidental losses, whether environmentally significant or not. Control of these losses requires an appreciation of the overall process system, as well as an understanding of what materials should, or should not, be discharged to the sewer, and the procedures to follow in the event of unforeseen difficulties.

Personnel training for control of accidental losses requires a specific training manual (or section within more general training manuals) and program, prepared by professionals who have the necessary knowledge of process operation and environmental protection. Separate training is required for shift operators, operating supervisors and maintenance personnel. Some pulp and paper producers have developed this expertise in-house, while others prefer to retain external consulting firms to prepare such manuals and training programs.

4. MILL EFFLUENTS

SUMMARY The principal sources of pollutants in kraft mill operations have been discussed in Section 3. The following section addresses aspects of the total mill effluent. The whole mill effluent is made up of the effluents from the various process equipment, plus cooling water etc. Accidental spills are an environmentally significant component of kraft mill effluents. Effective spill protection and an emergency response plan are a necessary part of any environmental protection program. All bleached kraft mill effluents contain significant quantities of suspended solids, BOD, resin acids and chlorinated organics. Although the concentrations of these substances are often relatively low, the effluent flows are larger than for most other industries, so that the mass flow of many low concentration contaminants can be significant. Flows vary widely from mill to mill, and tend to decrease with time, so the practice of reporting research results and setting regulations based on concentrations is scientifically unsound.

4.1 Average Conditions vs Spills

Mill effluent characteristics are constantly varying, and there is no simple, widely accepted way of summarising these variations. Ministry Control Orders are generally based on 30 day moving averages, which is an acceptable practical simplification for most regulatory purposes, as well as for the evaluation of medium and long term environmental impacts.

However, short term effects on receiving waters are often more dependent on "spills", which are unusually high discharges of one or more pollutants due to equipment or human failure. It is not easy to regulate spills, since their very nature as unpredictable events defies the development of practical regulations. Spill control depends mostly on good engineering practice in designing the mill, on the quality of the spill protection systems discussed in Section 3.8, and on good operating practices, operator training etc.

An emergency response plan exists at all mills to deal with major breakdowns of production equipment, and a response mechanism for spills should be integrated with it. The objective is to ensure that appropriate action is taken in response to environmental accidents, with timely decisions taken by responsible members of mill staff. Ideally, instrumentation should be installed to detect all potential spills, and warn the appropriate mill operator. This is impracticable with current technology, but it is practical to detect spills of black liquor, which is the most common spill problem, by monitoring effluent conductivity at strategic points. This, or equally effective technology, should be installed in all kraft mills.

The extent of spill prevention measures required is highly dependent on the location of the mill. At one extreme, a mill without biological treatment on a relatively small river would require quite advanced spill protection, whereas a mill with long-retention effluent treatment system discharging to a large lake or river might require only a relatively simple system.

The practical legislative approaches are the following.

Require that mills maintain sufficiently comprehensive records to analyse the causes of spills and take preventative action for the future.

Control Orders should contain a requirement for the mill to present an emergency response plan.

Where known hazards exist, install emergency catch-basins, to allow mill operating personnel sufficient time to take appropriate action. Classic examples are the safety dykes around oil storage tanks. Spill hazards specific to mill departments are discussed in Section 3.8

4.2 Effluent Flow

The pulp industry discharges effluent volumes which are much greater than most other industries, so that apparently low concentrations of pollutants can be significant in some cases. The effluent flow has no significant environmental effect in itself, but it is generally true in the pulp industry that process modifications which reduce effluent flow, also reduce the mass of pollutants discharged.

There has been a steady trend towards reducing the effluent flows for at least 40 years, but data from the early 1970's are useful for our purpose since that was the time when the fish lethality test was designed. In 1970, the average bleached kraft mill in Ontario discharged about 250 m^3/tonne pulp, whereas in 1986 the average was approximately 120 m^3/tonne pulp. The effluent flows can be expected to drop steadily as more modern equipment is installed in the mills and where mills modify the bleach plant substantially to reduce discharges of organically bound chlorine.

Environmental control regulations which are based on concentrations of pollutants in the effluent generally tend to discourage the implementation of environmental protection measures in pulp mills, and are therefore undesirable in most circumstances. The most obvious case is the current practice of regulating the acute lethality of effluents to fish, which is a measure of the *concentration* of toxic substances in the effluent. This is addressed in some detail in Section 7.5

We are disturbed by the current trend in the MISA program which seems likely to lead to regulation of a wide variety of chemical substances based on their concentrations in mill effluents. This will be a disincentive to mills to implement process modifications which reduce effluent flow, although in almost all cases in the kraft industry, any decrease in effluent is accompanied by a reduction in the mass flow of one or more pollutants. Although the MISA program will measure volume of discharge, and states an intention to regulate by both concentration and mass discharge, we fear that the multi-chemical of concentration will hamper progress.

4.3 Suspended Solids

SUMMARY Suspended solids were probably the most significant pollutants discharged by mills prior to 1960, but have been reduced to insignificance in most mills in Ontario. All Ontario kraft mills have primary waste treatment to take out suspended solids, and all mills are meeting provincial limits for discharge of solids. Loadings range from 2.9 to almost 14 tonnes per day at the various mills (Table 6.2). Although those are appreciable amounts, they do not seem to be causing problems. It might be noted that in the old days there were severe problems with mats of fibre accumulating on the bottom of rivers and lakes (Dymond and Delaporte 1952).

Fibre can cause acute lethality to fish, but only at unrealistically high concentrations. Softwood kraft fibres at 2,000 mg/L caused some mortality of fathead minnows in four days (Smith et al. 1965). However the more likely effect of excessive fibre is blanketing of the bottom of the waterbody that receives them, with consequent destruction of habitat for the normal bottom-living animals, and such effects were

demonstrated in the old days (Dymond and Delaporte 1952). If mats of fibre were formed on the bottom, slow decomposition could result in anoxic conditions in the layer, with formation of sulfides and other toxic gases.

There is no need for such situations to be created nowadays, and in general they are not. All Ontario kraft mills have installed effective in-plant measures and external primary treatment systems to remove most of the fibres and other settleable solids.

4.4 BOD

Biochemical Oxygen Demand (BOD) is a widely used measure of the tendency of an effluent to consume dissolved oxygen from a receiving water by natural biochemical degradation.

BOD is accepted internationally as a useful measure of the amount of degradable matter in an effluent, although it was developed for very different conditions from the rivers and lakes of Ontario. The concept and original test procedures date from the turn of the century, when BOD was used by investigators of environmental problems in England. The test involves sealing an effluent sample in a bottle under precisely defined conditions for a fixed period of time, and measuring the amount of the dissolved oxygen in the water which has been consumed at the end of the period. The English workers proposed a period of 5 days, since they considered that all effluents in England reached the sea within 5 days. Of course, this is far from true in Ontario. The test conditions and procedures are described in detail in many text books.

It is conventional to run the BOD test for 5 days in North America, hence the term "BOD_5". All references to BOD in this report are to the five day BOD, unless otherwise noted. BOD_7 is commonly used in Scandinavia, and caution is required when comparing reported data from these countries. The BOD_7 of any one effluent will generally be in the order of 15% higher than BOD_5, but it is impossible to develop a fixed conversion factor because of the varying constituents of waste waters.

The name of the test implies that chemical actions are not involved in BOD, but chemicals commonly found in kraft mills can have a significant effect on BOD. Sodium sulphide exerts an oxygen demand, under the conditions of the BOD analysis, of approximately 0.75 kg O_2/kg Na_2S. Leaks of white liquor, green liquor or weak-wash can therefore increase the BOD of a mill's effluent.

Chlorates can have the reverse effect on mill BOD, since they can give up oxygen under the conditions of the BOD test. Although sodium chlorate is used in most bleached kraft mills to produce chlorine dioxide, significant leaks are rare. However, up to about 3 kg of chlorates per tonne pulp can be discharged in effluents of mills using high chlorine dioxide substitution.

The BOD test indicates the oxygen demand of an effluent under certain defined conditions, but extrapolation of BOD laboratory data to predict the effect of the effluent on the dissolved oxygen levels in the receiving water is a complex task for experts.

It is easy to over-emphasise the importance of BOD as a measure of kraft mill effluent quality. By definition, only biodegradable substances will be measured in the BOD test, and persistent chemicals will normally have no influence on the measurement. Toxic heavy metals will reduce the measured BOD if not carefully considered in the analytical technique.

Most material which exerts an oxygen demand under the conditions of the classic BOD test, will degrade harmlessly in the receiving water within a few days. Providing that this degradation does not cause an unacceptable reduction in dissolved oxygen concentrations or release an over-supply of algal nutrients, the **BOD in itself is of little environmental significance.**

Part of the value of basing regulations on BOD has been that it served as a "catch-all" for organic material in general. Any regulation or effluent treatment process which reduces BOD will also reduce the general organic content of the waste water. However, it must be recognised that more specific controls are required if problems such as organochlorine are to be resolved.

The persistent compounds found in kraft mill effluent, whether toxic or not, will generally have no effect on the BOD test, and will therefore pass undetected by it.

4.5 Resin and Fatty Acids

Resin acids in kraft mill effluents contribute a major proportion of the acute lethality that may show up in the toxicity monitoring. However these substances decompose fairly readily and do not pose a major persistent toxicity problem. Fatty acids contribute a smaller amount to the toxicity of the effluent, and are decomposed quite readily in biological treatments systems or the natural environment.

Traditional biological treatment systems remove a substantial proportion of the resin acids, but mill experience has demonstrated that it is difficult or impossible to reduce the acute lethality of kraft mill effluents containing high concentrations of resin acids. Fatty acids are generally removed very efficiently by conventional biological treatment systems.

These materials are discussed in more detail in section 8.9 of this report

4.6 Reduced Sulfur Compounds

Reduced sulphur compounds including hydrogen sulphide, methyl mercaptan and various methyl sulphides are commonly found in untreated whole mill effluents in sufficient concentrations to taint fish and drinking water, and in some cases, have a major negative effect on acute lethality to fish.

If the effluent is biologically treated, the reduced sulphur compounds are stripped from the water quite efficiently, so they have no significant effect on the receiving water. However, many mills have an ambient odour problem up to a few kilometres away from effluent treatment systems.

Where the contaminated condensates in the mill have been stripped as discussed in Section 3.4 , the concentration of reduced sulphur compounds in the effluent can be expected to be environmentally insignificant.

Condensates from the evaporators and digesters (Cook et al. 1973), are known sources of tainting chemicals, and are estimated to contribute 20% of tainting properties of a bleached kraft mill (Blackwell et al. 1979).

4.7 Chlorates

In most mills, the chlorate content of the effluent is insignificant, but where a high proportion of the chlorine required in the chlorination stage of the bleach plant is replaced by chlorine dioxide substitution as described in Section 3.3.10, then up to about 3 kg chlorate per tonne pulp may be found in untreated waste waters.

The environmental effects are little documented, but the Committee for the Gulf of Bothnia (1987) indicated that adverse effects had been noted on the marine alga called bladder wrack. There are no reports of harm to freshwater algae.

Chlorate is readily converted to chloride in biological treatment systems. Ekstrom (1987) reported 90% removal at the Nymolla mill in Sweden, so it seems probable that it is reduced naturally in receiving waters in the case of mills which do not have biological treatment systems.

We do not consider chlorate discharges to be a serious environmental problem, although they will almost certainly increase since the current trend toward adopting high chlorine dioxide substitution to reduce TOCl discharges will probably accelerate in the near term.

4.8 Chlorinated Organics

A vast number of chlorinated organic chemicals are produced by bleaching in kraft mills, and are commonly known as organochlorines. A variety of analytical procedures are used to determine the amounts, including Total Organically bound Chlorine (TOCl), AOX, TOX (Total Organic Halide), POX, etc. Hundreds of organochlorines have been identified in bleach plant waste, but they represent only a small proportion of the total weight of chlorinated organic compounds discharged. There has been considerable concern expressed about the long term environmental effects of these substances in recent years, and some specific compounds of the dioxin group have attracted extensive media coverage.

Chlorinated organics are discussed at length in Sections 9 and 10, while methods of reducing their discharge are discussed in Section 3.

5. EXTERNAL EFFLUENT TREATMENT PROCESSES

SUMMARY The liquid effluent leaving a mill may require treatment before discharge to a body of water or watercourse. Depending on the untreated effluent characteristics and regulatory requirements, primary, treatment is usually required and secondary treatment may be required to reduce the impact of the treated effluent to acceptable levels for the specific environment where the mill is located. In most cases, the available external treatment technology improves the effluent by separating and concentrating some of the pollutants in a side stream, usually as a sludge but occasionally as a gas. Environmentally acceptable disposal of this side stream should be an integral part of the treatment process. In this respect , the long retention systems (aerated lagoons) are markedly superior to the many short retention systems. The general trend in the pulp industry is to use the in-plant techniques discussed in Section 3 to improve effluent quality, and reduce or even eliminate the need for external effluent treatment. In many mills, external effluent treatment processes are installed to treat part or all of the effluent from the mill. Reliability is the most important characteristic of external treatment systems if optimum environmental protection is to be achieved, so long retention systems have an inherent advantage over short retention systems.

External effluent treatment systems are conceptually simpler than the in-plant environmental protection measures discussed in Section 3, and are easier to specify in control orders and to regulate. The long retention systems (sedimentation basins and/or aerated lagoons) provide a buffer, which reduces the risk of a serious accidental spill causing environmental damage. On the other hand, short retention external treatment systems can raise the risk of environmental accidents because they are normally the principal component in the mill's water pollution control system, so that effluent quality is degraded spectacularly when they fail. The track record of short retention systems in US pulp mills has been studded with loss of treatment efficiency several times per year, due to unforeseen variations in mill raw effluent.

5.1 Pretreatment

Common pretreatment methods are grit and debris removal and effluent screening. Inorganic ash, grit from the wood preparation process, sand, and gravel usually must be removed from the waste effluents to reduce abrasion and prevent damage to pumps, piping and solids dewatering equipment.

A second important pretreatment process is the neutralisation of mill effluent. Not only will the pH of the wastewater affect conditions in the receiving streams, but extreme pH can cause severe equipment corrosion and adversely affect secondary treatment operation. Effluent pH should normally be between 6.5 and 8.0 to prevent disturbances to secondary biological treatment systems. The pH also has a strong effect on measured toxicity.

In bleached kraft pulp mills, effluent neutralisation can be achieved, to a large degree, by the use of waste chemicals and appropriate mixing of selected effluent streams. Lime mud from the lime kiln scrubber is added to the acid sewer at a controlled rate to achieve coarse upward adjustment of the pH. Following mixing with the alkaline sewer, which further raises the pH, final trim can be accomplished by the addition of acid and/or caustic if necessary.

5.2 Primary Treatment

This process removes 80 to 95% of the settleable portion of the suspended solids. The balance of the suspended solids, or unsettleable portion, consisting of colloidal or very fine material passes through the system. The settling aids or floculating chemicals added have included alum, ferric chloride and polyelectrolyte, but these are relatively ineffective in kraft mill effluents. Since part of the effluent BOD is related to the suspended solids in the effluent, primary treatment normally results in a reduction of about 10% of the total BOD.

Commonly primary treatment is accomplished in a gravity clarifier, which consists of a circular tank equipped with sludge removal rakes. The effluent is fed in at the centre and flows radially to the overflow weir located at the periphery. Settled solids deposited on the clarifier floor are raked to the centre by the rotating mechanical raking system and are drawn off and dewatered prior to disposal.

Alternatively settling basins may be utilised. They are usually constructed by excavation-and-fill earthworks with concrete inlet and outlet structures. They are normally designed with 6 to 24 hours retention time, allowing settleable solids to deposit on the floor of the basin. They may be lined with clay or a membrane to reduce seepage into the ground. Cleanout of the basins is accomplished with earth moving equipment. Although they are low in initial cost, settling basins may be costly to clean since there is no convenient means of removing water from the sludge prior to disposal. However they are very reliable if properly constructed since they do not rely on mechanical equipment. Where site conditions are suitable, the cleanout cost is lower than the cost of operating a primary clarifier. In newer installations, settling basins are often used as a back-up to primary treatment system for the gravity clarification processes, doubling as a spill basin when two or more are available.

Sludge produced by a primary treatment clarifier is normally dewatered on belt presses or vacuum filters which raise the sludge consistency from about 2% to 20 to 40%. In some mills where primary sludge is burned along with hog fuel in the power boiler, a further stage of dewatering in a cone or V-press is installed to raise dryness by an additional 5 to 15 percentage points.

In the past it was fairly common practice to incinerate the sludge recovered from primary treatment systems, since it consisted largely of wood fibres and bark. However, as mills have taken measures to reduce fibre losses,and have replaced wet debarking systems with dry ones, the proportion of combustible matter in the primary sludge has decreased markedly, so that incineration is becoming less practical.

Disadvantages associated with burning primary treatment sludge include additional abrasive wear on boiler internal parts, and possible slagging problems caused by low melting point components of the inerts in the sludge.

It has been reported that a significant proportion of the 2378 TCDD generated in the bleaching process is contained in wastewater sludges (Amendola et al. 1987). However, the analyses were performed on combined sludges from primary treatment and activated sludge secondary treatment systems, whereas in some Ontario mills the bleach plant effluents by-pass the primary treatment system, so it is unlikely that in those mills there are measurable quantities of 2378 TCDD or other chlorinated organic compounds in these primary system sludges.

However, in the case of mills where some of the bleach plant effluent passes through the primary treatment system, then the sludges probably contain measurable quantities of organochlorines, including the chlorinated dioxins.

5.3 Secondary Treatment

Secondary treatment is designed to remove BOD associated with the dissolved organic materials. The aerated lagoon has been almost universally adopted by mills in the Canadian pulp and paper industry which have secondary treatment systems. Other available methods include activated sludge using either air or oxygen, rotating biological contactors, trickling filters, and anaerobic systems, but these are less reliable, sensitive to shock loads, or more expensive.

The objectives of secondary treatment are normally to reduce the BOD by from 70% to 95% and to render the effluent non-lethal to fish, as defined in the effluent regulations. A biological treatment process can convert much of the organic material in mill effluent into water, carbon dioxide or organic solids. In some cases, it may be necessary to install equipment to dewater these solids and dispose of them in an environmentally acceptable manner and this part of the treatment process requires as much design and operating effort as the principal biological reaction section.

Biological treatment processes utilise naturally occurring micro-organisms to convert organic material to environmentally benign materials. The fundamental mechanisms have been discussed at length in many textbooks, and the following explanation is intended only to provide an appreciation of the key factors that affect the design and operation of pulp and paper industry waste treatment systems. Since essentially all systems in use for kraft mills in Canada are aerobic (operate in the presence of oxygen) the following discussion excludes anaerobic processes.

The micro-organisms are a mixture of bacteria, algae, fungi, protozoa, and other forms of life, which continually change to adapt to the effluent characteristics and conditions in the reaction vessel. Bacteria predominate, so their characteristics must be considered when examining the performance of biological waste treatment systems. The majority are from 0.001 to 0.005 mm in size, and they are surrounded by a cytoplasmic membrane through which all organic molecules, which the treatment system is expected to remove from the effluent, must pass. The materials in kraft mill effluents which cause the BOD and the toxic properties are primarily organic compounds and have quite a large range of molecular weights, so that there is a tendency for the smaller molecules to be treated preferentially, accounting for the characteristic tendency for biological treatment systems to be more efficient in the treatment of low molecular weight pollutants, such as methanol , than in treating the high molecular weight materials, such as chlorinated lignins.

Although the micro-organisms can adapt to changes in effluent quality, it is not uncommon for pulp industry discharges to change more quickly than the micro-organisms can react, which can cause abrupt reductions in the population and the subsequent loss of treatment efficiency.

Essentially, operating the biological treatment process consists of creating the appropriate conditions for a healthy population of micro-organisms to develop and feed on the organic matter in the effluent. Most of the published data and textbooks concerning the design and operation of biological treatment systems, concern municipal sewage. The failure of many pulp industry systems to perform as desired can be traced to the use of municipal treatment system design parameters, which are generally inappropriate for pulp industry wastes. The principal parameters are retention time, pH, temperature, dissolved oxygen, mixing energy and supply of sufficient nutrient material.

The maximum acceptable operating temperature, for a biological treatment system, is about 35°C. In the case of short retention time systems (under 12 hours) this may require a cooling tower for pulp mill effluent,

particularly since the current trend to reduce effluent flows by extensive in-plant recycle generally raises effluent temperatures.

Low temperatures hinder the biological reactions necessary for effective effluent treatment, and this must be considered in designing the longer retention time systems (over about 48 hours) where winter conditions are severe. Experience in Canada has shown that predictions in much of the American literature of complete failure of biological treatment processes in winter are not applicable to pulp industry effluents. Generally the high effluent temperature combined with the characteristic foam blanket prevents the temperature in the treatment systems from dropping to unacceptable levels, although efficiencies are normally lower in winter than in summer.

Kraft industry effluents are usually deficient in nitrogen and phosphorus, so these materials are added as required to maintain treatment system efficiency. Sufficient carbon is always available, since the objective of the treatment system is normally to remove the organic carbon compounds from the effluent. Oxygen must be also supplied by mechanical devices, most commonly surface aerators. Some aerated lagoons can treat kraft mill effluents successfully without adding phosphorus or nitrogen, particularly where retention times substantially exceeds 5 days. In general, BOD removal efficiency in kraft mill aerated lagoons can be expected to drop by a few percentage points if there are no nutrients added to the raw effluent.

However, high rate biological treatment processes, such as activated sludge, tend to require substantially more nutrients than aerated lagoons.

Biological treatment systems reduce the quantity of chlorinated organic compounds discharged, by about 35%. (Bryant and Amy 1987)

The concentrations of low-molecular-weight compounds (under 1000) are reduced substantially in effluents treated in biological treatment systems. (Bryant and Amy 1987). In some cases, such as methanol, the organic compounds are degraded into environmentally harmless carbon dioxide and water, whereas other compounds combine with the sludges in the treatment system, so that the "efficiency" of reducing their concentration in the effluent is a misnomer, since it represents merely the conversion of a liquid effluent problem into a solid waste disposal problem. In such cases, the fate of the sludges formed must be considered in evaluating the efficiency of the treatment system. Some low molecular weight compounds such as chloroform are simply stripped out or released to the atmosphere.

Conventional biological treatment systems are somewhat less efficient in reducing the concentrations of higher (over 1000) molecular weight organic compounds in bleached kraft mill effluents. By definition these compounds which persist in the environment, are generally resistant to degradation in biological treatment systems. Where an improvement in effluent quality can be achieved with respect to high molecular weight organic compounds, it is sometimes due to their being retained in the sludges formed in the treatment systems. Environmentally sound disposal of this material may therefore be a problem, and should be carefully analysed in evaluating any secondary treatment system.

Incineration of these secondary treatment sludges is rarely practiced, and is relatively expensive and demand significant energy due to the difficulty of dewatering . In the case of the highly persistent and toxic materials, of which 2378 TCDD is probably the most extreme, limited information from municipal waste incineration research indicates that this sludge can be incinerated safely provided that suitable

protective measures are implemented. This will cost much more than the "simple" incineration referred to above but significant engineering studies will be required to define actual capital and operating costs.

In all aerobic biological treatment systems, there is a tendency to strip out the reduced sulphur gases (TRS) which are the principal contributors to the classic kraft mill odour. Most of these travel from the mill's pulping system to the effluent treatment system with the contaminated condensates from the digesters and black liquor evaporators, as indicated in Figure 3.2. If the mill has neither a steam stripper (as shown in Figure 3.2), nor an air stripper, then the quantities of TRS gases emitted to the atmosphere at the secondary treatment system are sufficient to cause a marked, disagreeable odour for distances up to a few miles from the plant. Where a stripper is installed and operating efficiently, the odour problem is either very local or non-existent.

Anaerobic digestion has been proposed for treatment of kraft mill waste waters, and there is an active research program underway. There are no full scale operations in the kraft industry and the technical feasibility remains to be proven on industrial scale. The concentrations of BOD in the wastes are relatively low compared with successful applications of anaerobic treatment to wastes from the food industry, which tends to lower the effect of anaerobic processes.

The foregoing general discussion of biological treatment applies to all aerobic systems, and further specific points are discussed below in the descriptions of the commonly used processes.

5.3.1 Aerated Lagoons

The three Ontario kraft mills with secondary treatment systems (Fort Frances, Dryden, Espanola) use aerated lagoons.

The aerated lagoon commonly provides a 3 to 10 day retention of the effluent where, in the presence of dissolved oxygen, nutrients and low concentrations of micro-organisms, the organic matter in the effluent is stabilised, and some of it is converted to carbon dioxide and water. The dissolved oxygen is replenished by electrically driven mechanical aerators on the lagoon surface (or in some cases by diffusers or mixers located on the lagoon bottom using air supplied through a piping system). The classical requirements of about five parts of nitrogen and one part phosphorous per 100 parts of BOD are frequently met by the addition of urea or ammonia and phosphoric acid in the initial months of lagoon operation to provide sufficient nutrients for optimum treatment efficiency. Experience shows that these nutrients recycle themselves in the lagoon sufficiently to render continuous addition unnecessary in many cases.

A large proportion of the suspended solids produced by the reaction settle in the lagoon and are consumed by auto-oxidation. One of the key factors in design and operation of aerated lagoons is to ensure that this actually takes place, to avoid the need for expensive and difficult cleanout operations, and creation of a sludge disposal problem. . Many lagoons are successful in this respect, but some are not, usually due to overloading or design deficiencies.

In comparison with the other secondary treatment methods aerated lagoons require a large area of land. However, the lagoons provide distinct advantages over higher rate systems which include:

ability to absorb shock loads of concentrated effluent without appreciable change in treatment efficiency;

little or no nutrient addition required except at initial start-up (hence little extra nutrient discharge to the receiving water);

lower net settleable solids generation, thus avoiding clarification processes and sludge disposal;

lower energy consumption due to avoidance of sludge handling;

better toxicity removal; and

higher reliability due to the simplicity of the mechanical equipment

Some of the acutely toxic components of pulp mill effluents degrade more slowly under the action of the biological organisms. The longer retention-time processes such as the aerated lagoon therefore provide better toxicity removal than short retention-time processes. This can be extremely important in terms of reducing the impact of effluent discharges on the fish and aquatic life of smaller watercourses.

Chlorinated organics can be removed by treatment in aerated lagoons. Norström (1987) estimates that only 20 to 30% of such compounds are removed, mostly those with low molecular weight.

Bryant et al. (1987ab) and Bryant and Amy (1988) showed that over 30% of non-volatile organochlorines and essentially all volatile organochlorines were removed in one operating bleached kraft mill aerated lagoon. They showed that 35% - 50% of organochlorines were removed in an aerated lagoon. We have assumed 35% for estimates in this report, and some recently received unpublished, independent data indicates that we are conservative.

Bryant and Amy (1988) also presented a balance showing that 90% of the non-volatile organochlorine removed was converted to inorganic form in the benthal sludge biomass in the lagoon. Personal communication with the authors indicated that these data were typical for several kraft mill lagoons that they had investigated.

Bryant and colleagues found that removal of the low molecular weight compounds was somewhat, but not substantially better than for high molecular weight (MWt. > 1000). The low-molecular-weight ones are the more acutely lethal ones, which is encouraging insofar as the effluent is concerned. There have been questions of how much of those substances is decomposed and how much is simply deposited in the sludge and could later cause problems, for example by getting into groundwater from landfill sites used for sludge disposal. This work indicates that aerated lagoons do indeed remove a portion of the organochlorines, but there is no evidence that high rate systems such as activated sludge do more than simply concentrate the organochlorines in the sludge.

The apparent difference between the estimates of Norström and Bryant estimation of the organochlorine removal efficiency is misleading. Norström's comments are based on the Sjostrom (1982) test for TOCl, whereas Bryant used the APHA TOX procedure. The TOCl method includes a one-week "stabilisation" period, which reduces the measured TOCl value by in the order of about 15% due to the loss of volatiles and to chemical reactions, whereas TOX analyses are performed on a fresh or frozen sample. However, the ageing process will have little or no effect on a sample of effluent which has already been stabilised by treatment in an aerated lagoon.

Thus a given sample of, say 100 mg/l TOX, would drop to 65 mg/l according to Bryant and colleagues, for a removal efficiency of 35%. The same sample would have 85 mg/l organochlorine according to the TOCl analysis, and would drop to 63 mg/l assuming a treatment efficiency of 25% as mentioned by Norström. Clearly, Norström and Bryant and colleagues are in close agreement, when one considers the differences in analytical procedures involved.

The aeration processes used in secondary treatment of pulp mill waste waters results in the creation of foam, which has a beneficial blanketing effect in retaining heat in lagoons in cold climates. This foam is normally removed prior to discharge of the treated effluent to the watercourse by using submerged outlets from the process and avoidance of foam-producing drops and partially filled pipe flows.

The foam on the surface of most kraft mill aerated lagoons is blown around by the wind, and deposited on surrounding land. The problem is generally quite localised, but does represent a significant objection to installation of aerated lagoons in or close to built-up areas, even where there is sufficient land available for construction of the facilities.

5.3.2 High Rate Biological Treatment

Several relatively short retention biological treatment processes are used for treatment of municipal sewage and a wide variety of industrial wastes. The traditional activated sludge process is by far the most common of those in the pulp industry, but rotating biological contactors, trickling filters, and extended aeration have all been used.

These high rate processes are characterised by very high concentrations of biologically active material which contacts with the organic wastes in the mill effluent for a relatively short time. The rate of BOD reduction is thus quite rapid, with treatment completed in 2 to 6 hours, resulting in much more compact installations. Generally, the higher the reaction rate, the more suspended solids are produced. To reduce the suspended solids in the effluent and sustain the biological process, the outlet effluent must be clarified and most of the sludge collected is returned to the treatment system inlet.

The excess sludge, in the order of 0.5 solids/kg BOD removed must be dewatered and disposed of effectively, which may require significant quantities of energy and chemicals, and which may cause some environmental problems. Dewatering and landfill disposal of the waste activated sludge would typically cost about $70/dry tonne, which corresponds to about $0.8/tonne bleached kraft pulp produced.

Activated sludge plants require more operating labour and technical staff than aerated lagoons, and we have calculated that this additional cost would be approximately $300,000/year for the type of activated sludge plant that may be installed in Ontario. This cost is virtually independent of the size of the plant. (All costs in Section 12 assume that aerated lagoons would be used wherever biological treatment is required, rather than activated sludge).

The activated sludge process for BOD reduction using either air or oxygen can be more economic than aerated lagoons where a suitable site land area is extremely expensive, or so far from the mill that effluent pumping costs exceed the above mentioned additional operating costs for an activated sludge system. Generally, it is more economic to pump effluent several miles to an aerated lagoon than to install an activated sludge secondary treatment system close to the mill

Several kraft mills, board mills and deinking plants in the US have adopted the activated sludge process for treatment of effluents and it is common in Finland. The process is little used in Canada, and the only application in Ontario paper industry is in the newsprint mill in Thorold.

In Canada most mills have sufficient land available for aerated lagoons, and mills prefer their superior reliability and toxicity reduction capabilities relative to activated sludge systems. High rate biological systems were generally developed for treatment of municipal effluents. In theory they are capable of higher BOD removal efficiencies than the low rate aerated lagoon systems, but operating experience in the pulp industry has been disappointing, principally due to the wide variations in raw effluent quality which are characteristic of these wastes. There is much evidence that toxicity removal of the activated sludge process is generally inferior to that of a low rate system.

Site specific technical conditions may of course override the foregoing generalised comments.

5.3.3 Physico-Chemical Processes

Lime is successful in removing toxicity from some waste streams but not others (Naish and Sandilands 1977). Alum or ferric chloride will make bleached kraft mill effluent non-lethal (Coss and Wilson 1975). However neither of those methods of precipitating material would likely meet with much favour because of the disposal problem with the sludge produced.

5.3.4 Fraser Process

Treatment of bleach plant effluents with small amounts of sulfur dioxide has been shown to reduce the toxicity of bleached kraft mill (Betts and Wilson 1966). The procedure was known as the "Fraser Process"

It has been shown independently that sulphur dioxide reduces toxicity and mutagenicity in bleach plant effluents (Donnini 1981, 1982). However, that may not result in a decrease in toxicity of the combined mill effluent (Donnini et al. 1985). Although this method was suggested over 20 years ago it does not seem to have become routinely used.

5.3.5 Ozone

Ozone treatment of unbleached kraft mill effluent successfully removed toxicity if the suspended solids had been removed previously. The treatment had little effect on BOD and colour (Dorica and Wong 1979). Other investigators found just the opposite; ozonation of bleached kraft mill effluent was of benefit in removing colour, had some effect on BOD, but did not reduce toxicity (Ng 1976).

5.3.6 Foam Separation

Foam separation has been proven at the pilot-plant scale as a method of dealing with toxicity, but is not in actual use at Canadian mills, nor do we recommend it. In this procedure, a foam would be generated purposely, and much of the toxicity of an effluent would be concentrated in that foam. The liquid portion, now non-lethal to fish, might be released without further treatment. The foam would then be collapsed and biologically treated to remove its toxicity. The advantage of the process would be in avoiding the cost

of a large lagoon system to treat all the waste, for example if suitable land was not available. However the foam separation process is as expensive as lagooning or more so, and the procedure does not improve the BOD of the liquid effluent (Ng et al. 1979). The foam does indeed collect toxicants, and may be expected to have an LC50 of 0.01% to 0.02% (Servizi et al. 1979). In one foam assessed by Servizi et al., 70% of the toxicity was from resin acids, and 30% was from neutral diterpines (alcohols, aldehydes, and ketones).

5.4 Tertiary Treatment

The components remaining in the effluent after primary and secondary treatment include residual suspended solids, residual BOD, nutrient, colour, organochlorines and materials which may cause lethal or sublethal toxicity, odour, and taste.

Tertiary treatment can remove further proportions of these remaining components, but very few have been used for the pulp mill effluent anywhere in the world, because they have been considered environmentally unnecessary. They are generally costly to operate, and include:

activated carbon absorption;

massive lime treatment; and

foam separation.

5.5 Sanitary Effluents

Toilet, washroom and other office liquid wastes in newer mills are collected and treated in separate sanitary sewer systems. Treatment is by established municipal sewage treatment practice, frequently in a package plant, and following final chlorination, the sanitary waste may be added to the mill effluent for common disposal.

In older mills, sanitary sewage is added to the nearest sewer or trench which can potentially result in pollution of the watercourse with pathogenic bacteria. Conventional treatment of these bacteria is by chlorination or ozonation, but this is not practical because of high chemical demands of the relatively large effluent flows. Many mills are steadily modifying their sanitary sewer systems in accordance with modern practice and this approach is recommended.

5.6 Outfalls and Treated Effluent Disposal

The method of discharging a mill effluent to the receiving water has a significant effect on its environmental impact. It is usually preferable to dilute the effluent as quickly as possible after discharge, and always desirable to take measures to reduce or eliminate visible foam and colour on the surface of the receiving water. Refer to section 7.4.1 for discussion of mixing zones.

The purpose of a good diffusing outfall is not simply "out of sight, out of mind" but to avoid local accumulations of high concentrations of materials with short-term deleterious effects. Persistent or bioaccumulative toxicants must be eliminated before the effluent is discharged; it is of little benefit to the environment to dilute them.

The outfall location must be carefully selected, and in some cases it could be more effective to expend resources on the construction of an environmentally effective outfall than on a waste treatment plant. An obvious example could be a mill located near the mouth of a small river, where an outfall line, perhaps as much as several kilometres long, would discharge the effluent to the sea or other large waterbody rather than to the river.That could be more effective in minimising environmental impact of the mill than a high degree of effluent treatment, followed by discharge to the small river.

Outfall selection and design is very site specific, so it is difficult to provide any general guidelines. The efficiency of dilution must be evaluated, with due consideration of the effects of currents and density differences between the effluent and the receiving waters. In addition to satisfying environmental criteria, the outfall site must be suitable for the construction of a structurally sound installation. The performance of an outfall is very reliable (more so than any effluent treatment system), but structural failures are sometimes very difficult to correct, particularly in winter conditions.

6. MILLS IN ONTARIO AND ELSEWHERE:

In this section of the study the aim is two-fold:

first to provide the reader with a description of the industry in Ontario in terms of the types of production and effluent treatment systems installed in kraft mill; and

second, to provide a comparative analysis of effluent treatment systems currently employed in mills in other major producing areas.

6.1 The Ontario Kraft Industry

SUMMARY. (1) There are 27 mills in the Ontario pulp and paper industry, of which 9 use the kraft process to produce pulp. (2) Production of kraft pulp in Ontario takes place in both an integrated and a non-integrated environment. In an integrated environment, pulp is produced either wholly or partially to meet the company's own chemical pulp requirements for the manufacture of paper products. E.B. Eddy's Espanola mill is a good example of an integrated operation: pulp is produced both to meet the company's demand for chemical paper grade pulp used in the manufacture of paper products and for sale as market pulp. Domtar, which is one of the largest producers of kraft pulp in the province, uses all of the production from the mills located at Cornwall and Red Rock to meet internal demands for chemical pulp. In this case, pulp is not sold on the open market. In the non-integrated environment, all of the pulp produced is sold as market pulp. In Ontario, James River Marathon, Kimberly Clark (Terrace Bay) and Mallette Kraft and Power (Smooth Rock Falls) sell 100% of their output of pulp on the market.

The total annual capacity for producing chemical paper grade pulp in Ontario, based on 1986 mill operating environments, has been estimated as being equal to 2.66 million tonnes (CPPA 1987). This represents approximately 20% of Canadian total capacity. With respect to kraft pulp, we estimate that production in Ontario in 1986 was equal to between 2.2 - 2.3 million tonnes. (This figure has been estimated from mill sources and available published data.) Accurate data on the proportion of kraft pulp production in Ontario that can be classified as market pulp are not available. However, calculations based on CPPA (1987) indicate that the total capacity in Ontario in 1986 of all grades is close to 1 million tonnes. Analysis of individual company data indicates that market pulp production in 1986 was considerably higher than that. Market kraft pulp capacity estimated by using micro data for 1987 is roughly equal to 1.6 million tonnes. It should be noted that the proportion of market to total pulp production is not fixed. The amount of pulp produced for the market depends in part on the effective price for market pulp relative to the price prevailing for a range of paper products. If, for example, an integrated company is faced with a "low" effective price for market pulp and "high" prices for manufactured paper products, the company may be able to divert pulp ordinarily destined for sale on the market to internal use. Conversely, a "high" price for market pulp relative to prices for manufactured paper products will cause the quantity of market pulp to increase.

One of the features of the Canadian Pulp and Paper industry is that it is relatively highly integrated. In consequence domestic demand for market pulp is not very large. Because of this factor, in excess of 90% of market pulp production is sold to export markets, the most important of which is the United States. In

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1 The terms "kraft" and "sulphate" are used interchangeably in this report and throughout the literature

1986, 50.5% of total Canadian exports of bleached softwood kraft pulp were shipped to US markets compared with 13.6% to Japan and 19.2% to countries in the European Economic Community. With respect to the latter, West Germany, Italy, France and the United Kingdom are the most important individual markets (Statistics Canada, 65-202). Although detailed data is not available for the Ontario kraft sector, it is probable that a greater proportion of Ontario's exports of kraft pulp will be to US markets than is the case for the country as a whole. (This statement is based on an analysis of data supplied by mills, data contained in the Statistics Canada export data base for total exports originating in Ontario for all grades of pulp and on transport origination-destination data.)

The market for kraft pulp is extremely competitive. Although Canada is the world's largest producer of market pulp, accounting for 27-28% of world sales of chemical paper grade pulp (most of which is sulphate), Canadian producers do not have the ability to set market prices. Both US and Canadian anti-trust legislation broadly prohibit collusive behavior. Even in the absence of such statutory prohibitions, it is very unlikely that collusion would be possible or profitable given the large number of individual producers and the international nature of the markets involved.

The underlying production function for the kraft pulping process is typified by a high level of sunk and fixed costs. (Sunk costs are defined as those costs which would not necessarily be recovered if the firm, or a part of the firm, left the industry.) The presence of sunk costs is important since it means that the industry is not characterised by easy exit or entry conditions. In addition to the presence of sunk costs, a high proportion of the capital equipment has a very long physical life. These factors, together with the presence of important economies of scale and the relatively large number of separate producers world-wide, help explain the cyclical nature of the industry in the face of changes in the overall level of demand for pulp. In this context, it is not surprising that the effective real price for market pulp has fluctuated considerably during the last thirty years. In general, the pattern of industry price changes is typified by the following transmission mechanism: a period in which market demand for pulp is rising will lead to an increase in mill operating rates. If demand for pulp continues to rise, a point will be reached where mills are unable to increase the supply of pulp from existing facilities and the price of market pulp rises. A period in which prices are rising and mills are operating at - or very close - to full capacity is generally followed by an expansion of capacity, either by mills adding to the capacity of existing production facilities or by the construction of greenfield mills. The increase in capacity in recent expansion cycles has generally caused the supply curve to shift outward to such an extent that "official" or posted prices are reduced or that posted prices are discounted. The softness in price is accompanied by a decline in the operating rate as mills adjust to lower prices. If the decline in price is sufficiently large, producers with high variable costs relative to the rest of the industry will halt production, either on a temporary or permanent basis.

6.2 Ontario Kraft Industry Relative to the Rest of the World

SUMMARY. Production of kraft pulp in Ontario is estimated to be equal to between 2.2 - 2.3 million tonnes (1986). Production of market pulp in Ontario is shown to be around the 1.6 million tonnes level. Although Canada is the world's largest supplier of market pulp, Canadian producers do not have the power to determine market prices, and the pulp grades and quality produced must respond to this market.

Table 6.1 Production characteristics at Ontario's kraft mills. (Data from MOE files. and mill visits by authors)

Company	Location	Total Production Tonnes/day	Kraft Production Tonnes/day	Wood Species	Bleaching Sequence
Boise Cascade	Fort Frances	1135	550 kraft 350 full bleach 200 semi bleach	67% jack pine 16% spruce 9% poplar 8% black spruce	CdEoHD
Great Lakes	Dryden	1000	777 kraft (90% bleached)	55% Jackpine 45% black spruce (changing toward 40% hardwood)	CdEoHDED
Great Lakes	Thunder Bay	2280	1280 kraft AMill:580 softwood BMill:744 softwood 50/50% soft/hard 1140 t/d newsprint	70% jackpine 15% balsam 15% spruce Swd is 100% aspen	DcEoHDED DcEoDED
Domtar	Red Rock	800	50 t/d semi bleach 530 t/d kraft linerboard 200 t/d newsprint	5% aspen/birch 85% Jackpine 10% Spruce	CEH
Kimberly Clark	Terrace Bay	1160	All Bleached Kraft 790 softwood 370 hardwood	5% Balsam 30% Jackpine 65% blackspruce Swd is 100% poplar	DcEoHDED DcEoDED
James River	Marathon	435	435 Bleached	54% spruce 34% Jackpine 10% Poplar 2% balsam	CdEoHED
E.B. Eddy	Espanola	885	885 Bleached Kraft	46% Jackpine 8% spruce 45% birch/maple and poplar	OCdEHD OCdEoHD
Malette	Smooth Rock Falls	300	300 Bleached Kraft	65% blackspruce 35% jackpine	CdEoDED
Domtar	Cornwall	734	315 bleached kraft	100% hardwood	CdEoD

Table 6.1 provides summary information on principal products and production processes in the 9 Ontario kraft mills. The data indicate that the Ontario kraft sector's major product is fully bleached softwood kraft pulp. A small proportion of total production is in semi-bleached grades, almost all of which is non-market. Three mills are producing bleached hardwood pulp, two in combination with softwood pulp. Note that data are nominal, since exact values depend on reporting basis, and vary from day to day. Refer to Section 3.3.2 for definition of abbreviations on bleaching sequences.

Table 6.2 Effluent treatment and quality at Ontario's kraft mills. Effluent data from 1986 MOE reports, the remainder from mill visits in 1987 and 1988.

Company	Boise Cascade	Great Lakes	Great Lakes	Domtar	Kimberly Clark	James River	E.B. Eddy	Malette Kraft Power	Domtar
Location	F.Frances	Dryden	T. Bay	Red Rock	Ter. Bay	Marathon	Espanola	SM.R. Falls	Cornwall
Processes	Kraft Grdwood	Kraft Fine papers	Kraft Groundwood Sulphite	Kraft Groundwood Linerboard	Kraft	Kraft	Kraft Speciality paper	Kraft	Kraft Fine paper
1986 Effluent data									
Flow (1000 m^3/d)	69	75	216	91	110	64	112	53	101
BOD t/d	10.5	2.64	43	17	30	14	2.19	7	15.1
S.S. t/d	4.5	3.3	14	4	5.3	3	5.1	2.9	7.9
Current regulatory limits									
BOD t/d	15	-	5.5	23	42.7	15	3.6	9	27.7
SS t/d	7.5	5.6	14.0	5.5	7.5	6	-	4.5	*[2]
Control Measures									
Dry debarking	1/2 & 1/2	yes	yes	no	yes	yes	no	none	yes
Screen Sys. Closure	yes	yes	yes	no	yes	no	yes	no	no
Steam Stripping	no	yes	yes	yes	yes	no	yes	yes	yes
Eff. Neutralisation	yes	yes	yes	yes	In c.o.	no	yes	no	no
2ndary treatment	yes	yes	no	no	no	no	yes	no	no
Chlorine diox. subst	10%	5%	50%	0%	40%	4%	10%	13%	30%
Diffuser outfall	yes	yes	yes	no	no	yes	yes	yes	yes
Oxygen delig.	no	no	no	no	no	no	yes	no	no
Toxicity Monitoring									
MOE	yes	yes	yes	yes	yes	yes	yes	yes	yes
Company	4/yr	4/yr	4/yr	4/yr			1/mo	1/yr	4/yr
LC50	10-100%	10-100%	22-64%	45-100%	10-46%	12-15%	100%	18-40%	50-100%

2 *Domtar and the Ministry of the Environment were contesting the SS discharge limit for the Cornwall mill at the time of writing.*

Given that approximately 90% of the output of market kraft pulp is exported, the profitability of Canadian producers is strongly influenced by the value of the Canadian dollar relative to other currencies. In particular, a decline in the value of the Canadian dollar against its US counterpart will cause windfall gains for those Canadian producers heavily dependent on US markets. Conversely, a rise in the value of the Canadian dollar relative to the US dollar will cause windfall losses. A change in the value of the US and Canadian dollars relative to other major currencies is also of importance. For example, the recent drop in the value of the two North American currencies against most other major currencies has made it less attractive for Scandinavian producers to ship pulp into US markets and more attractive for Canadian producers to sell into European market and other markets.

Along with significant competition in major markets from traditional Scandinavian (mainly Swedish) suppliers - who account for 25% of total world sales of chemical paper grade pulp - Canadian exporters of kraft pulp face increasing competition in some markets from other European and Latin American producers. In recent years, there has been an increase in market pulp production from the latter two sources, particularly in bleached hardwood pulps (although production has increased significantly in Latin America, export levels have not changed greatly in recent years).

In addition to the above factors, production in CTMP grades has increased dramatically during the last five years relative to kraft capacity. Over the period 1976-1986 total wood pulp capacity in Canada increased at an average rate of 0.72%. Whereas capacity in sulphate grades increased at an annual rate of 1.5%, the increase in thermomechanical grades was equal to 27% per annum (CPPA 1987). There is every indication that this trend will continue. In Canada, for example, CTMP capacity will increase by 391,000 tonnes between now and 1989 (all of the increase will be accounted for by new mills in Alberta and Quebec). Kraft capacity is expected to remain constant in Ontario over the same period.

The fact that Ontario's output of market pulp as a proportion of world output has declined in recent years - and in all probability will continue to decline for the foreseeable future - should not be taken to be indicative that an Ontario location is uncompetitive vis-a-viz other locations. Anderson and Bonsor(1985) note that:

"The presence of favorable profit opportunities in Ontario's major pulp and paper manufacturing activities is certainly a **necessary condition** for investment and capacity expansion. But, as a primary manufacturing sector integrated backwards into timber supplies, newsprint, and kraft pulp production in Ontario also requires as a **necessary condition**, the presence of adequate provincial wood supplies at reasonable cost". (Original emphasis)

There is a very considerable body of evidence indicating that wood supplies in Ontario are a serious constraint on the addition of productive capacity (Reed Paper Inc. 1980). Indeed, the rapid expansion of capacity that took place in the 1970's (kraft pulp capacity increased by 80% from 1970 to 1980 and also expanded modestly in the early 1980's) has created a situation in which existing mills may face a wood supply problem in the immediate future, especially in softwoods.

Given the absence of wood supplies at reasonable cost f.o.b. the mill, it is not surprising that in a period where the demand for pulp has increased, Ontario's proportion of world, and Canadian, output has declined.

6.3 Effluent and Water Quality Considerations of Ontario Kraft Mills

6.3.1 Suspended Solids

All Ontario kraft mills have primary waste treatment to take out suspended solids, and all mills are meeting provincial limits for discharge of solids except that Cornwall is marginal. Loadings range from 2.9 to almost 14 tonnes per day at the various mills (Table 6.2). Although those are appreciable amounts, they do not seem to be causing pollution problems of a physical nature. Continued control is important, however, since persistent bioaccumulative toxicants tend to travel on particles, being poorly soluble in water.

It might be noted that in the past there were severe problems with mats of fibre accumulating on the bottom of rivers and lakes (Dymond and Delaporte 1952). Many mills dumped all bark and other solid waste to watercourses prior to 1960 so discharges were probably over 200 kg/t pulp, equivalent to 60-400 t/d of suspended solids for today's mills. A grab sample at the Espanola mill in 1949 showed just such values, of 60 tonnes per day for the relatively small mill, equivalent to at least 240 kg of suspended solids per tonne of pulp (Dymond and Delaporte 1952). Today's suspended solids are largely non-settleable in contrast to those discharged prior to the installation of primary treatment systems.

The history of suspended solids discharges by Ontario kraft mills shows that some mills have had major decreases in suspended solids since 1970 as summarised in Figure 6.1

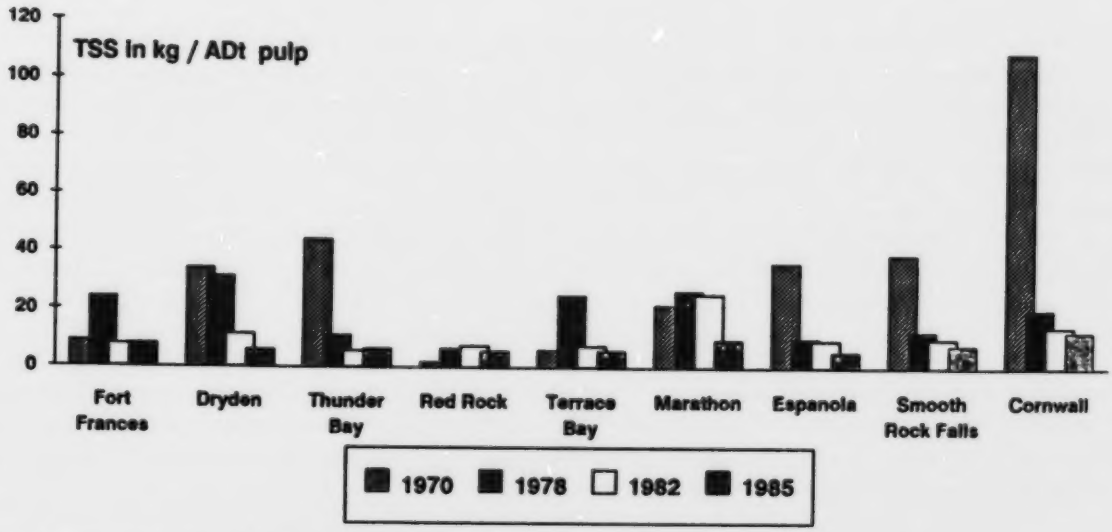

Figure 6.1 Historical suspended discharges in Ontario mills. Data from Environment Canada files.

6.3.2 Biochemical Oxygen Demand

SUMMARY. (1) BOD is one of the "traditional" kinds of pollution. The effect on ecosystems is to lower the dissolved oxygen. (2) Three Ontario kraft mills have secondary waste treatment, and in at least one case (Espanola) that has remedied previous problems of dissolved oxygen. Other mills do not have a problem because of large amounts of dilution water and effective diffusers on the outfall. (3) Some locations suffer damage from reduction of dissolved oxygen. The choices to remedy those problems are essentially in-plant control of losses, secondary waste treatment, or relocation of the effluent outfall. Although in-plant control has limited scope, regulations should encourage it, since that helps to reduce other pollutants such as toxic substances. (4) It is easy to regulate against BOD, and it is easy to follow the U.S.A. and require secondary treatment of all mill effluents. We do not suggest that approach. (5) The effluents from the 9 Ontario kraft mills have a combined oxygen demand that is equivalent to the raw sewage of 1.4 million people, and many of the effluents are as strong as raw sewage in their BOD. Nevertheless that total deoxygenating potential is trivial in the overall budget of the most frequent recipient, Lake Superior, delicate as that lake is. Accordingly we do not recommend any blanket requirement for secondary treatment for the purpose of reducing BOD. (6) We recommend stricter regulation as necessary to maintain favorable concentrations of dissolved oxygen in the particular local waterbodies at each mill-site.

BOD is simply a measure of the amount of organic matter in effluent or water, which can be decomposed by micro-organisms, using up oxygen from the water during that decomposition. The harmful aspect for fish and other clean-water organisms is the reduction in dissolved oxygen, so a BOD measurement is merely an estimate of the potential harm to aquatic ecosystems. Whether or not that potential is realized depends on the dilution available for the effluent, and on factors such as the re-oxygenation coefficient in rivers, temperature and the extent of other BOD discharges.

Historical Improvements

The BOD of Ontario kraft mill effluents currently meets the requirements of the MOE control orders in all cases (1986 data, Table 6.2). In some cases the BOD loading is greatly improved compared to a few decades ago. For example, in the classic survey of the Spanish River, Dymond and Delaporte (1952) reported 1949 a sample which showed that a small bleached kraft mill had a BOD loading of some 75 kg for each tonne of product (Table 6.3). In our experience, workers of that era usually underestimated kraft mill BOD.

Table 6.3 Change in a mill effluent 1949 - 1986.

Year	BK production tonnes/day	BOD loading tonnes/day	BOD, kg/tonne of product
1949	200	15	75
1986	885	2.2	2.5

The 1949 calculation ignores a minor output of groundwood. In 1986 the production was much higher, but the BOD loading was reduced by 85%, representing 30-fold improvement in loading per tonne of product! Oxygen concentrations in the river improved similarly. From summer minima of 4 to 5.6 mg O_2/L in the early 1950s (concentrations that are in the vicinity of our Low Level of Protection, see Section 11), the oxygen minima increased in 1984-85 to 7.8 mg/L (meeting our High Level of Protection).

It is gratifying to see such improvements at a particular mill. It was gratifying during a visit in July 1987 to see local people fishing from a boat just downstream of the mill; presumably they had reasonable expectations of edible fish in that location. It was gratifying to reflect that the same mill had one of the lowest ratings for output of chlorinated organic chemicals, of any fully bleached kraft mill in Canada. It was gratifying to learn that the mill was profitable.

The more recent history of BOD discharges (Figure 6.2.) shows that most mills have made improvements.

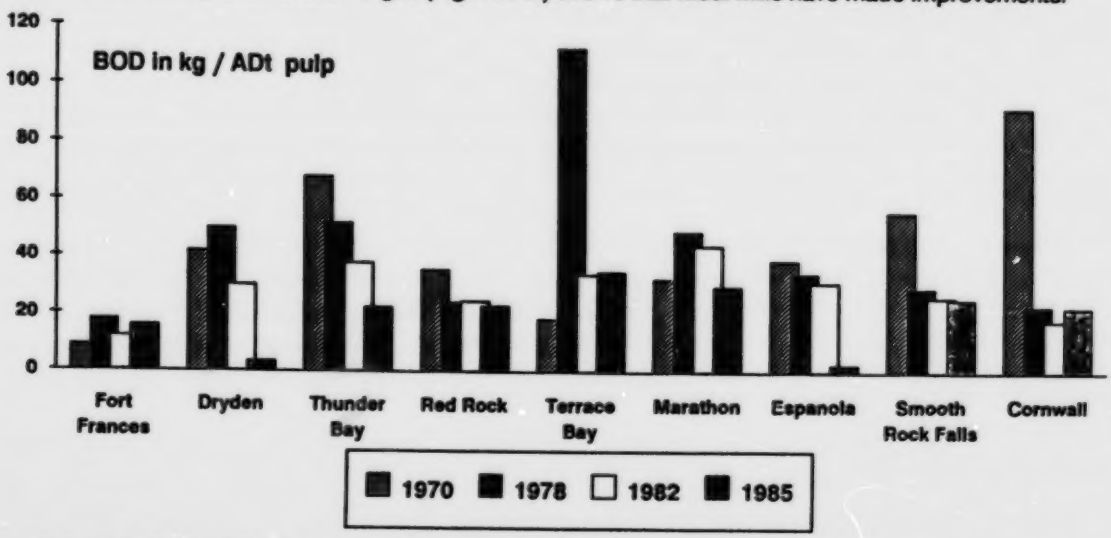

Figure 6.2 Historical BOD discharges in Ontario mills. Source: Environment Canada files

Population equivalents

Prima facia, we are shocked by the BOD loading from most Ontario kraft mills and by the strength of their effluents, although analysis of the data below presents a different picture. We list in Table 6.4 , the loadings and strengths of effluents from the 9 Ontario mills, as calculated from data in Table 6.2. The first column represents tonnes of oxygen required per day to satisfy the BOD, the second column represents the "population equivalent", i.e. the equivalent BOD from raw sewage of a town with the listed population. The third column is the actual strength of the wastewater in mg/L of BOD, and we have inserted for comparison, the strengths of well-treated municipal waste and of raw municipal waste.

Table 6.4 Pollution equivalents of the nine Ontario kraft mill effluents in terms of potential deoxygenation of receiving water.

	BOD, tonnes/d	Population equivalent	Effluent BOD,mg/L
	2.2	22,000	19
		Well-treated domestic sewage:	20
	2.6	26,000	35
	7.1	71,000	133
	15.1	151,000	150
	10.5	105,000	151
	17.2	172,000	188
	43.1	431,000	200
		Average strength, raw municipal sewage:	210.
	14.3	143,000	222
	29.6	296,000	268
Total	142.	1,420,000 **Average**	152

It is sobering that the mill effluents have a total oxygen demand equivalent to the raw sewage of 1.4 million people, and that many of the effluents have the strength of such raw sewage. Only one effluent is down at the well-treated level, and that is the one mentioned favorably in connection with the Spanish River. The third set of mill values (down from the top) represents the outflow from an aerated lagoon but obviously the lagoon was not functioning very well, to produce an effluent with BOD of 133 mg/L.

The municipal water pollution control plant for Thunder Bay can be offered as a comparison. It serves 102,000 people and takes in raw waste with a BOD of 14 tonnes per day. After treatment, the plant discharges to Lake Superior an effluent with 4.9 tonnes per day of oxygen demand (Romanick 1987). The kraft mill in town discharges 43 tonnes per day, almost 10 times as much BOD. Ignoring the sanitary aspects, it is rather obvious which source deserves the most regulatory attention, if one is concerned about the discharge of deoxygenating wastes to the lake.

Effects on Lake Superior and smaller waterbodies

We attempted to assess the BOD discharge of the mills from a broad or "global" viewpoint. We were concerned that 4 mills discharge to Lake Superior or arms of it, because this is a delicate, soft-water, oligotrophic lake. Also it is a lake that would be slow to cleanse itself of any pollution problem because of a very slow turnover time (rate of replenishment of water). It would require 550 years of river and rainfall inputs to replace 95% of the water molecules in Lake Superior, compared to only 9 years for the same exchange in Lake Erie.

However it appears that the BOD is of trivial importance for the oxygen budget of Lake Superior as a whole. Even if all 9 mills discharged to Lake Superior, the total daily oxygen demand of 142 tonnes would only require the oxygen from a cube of water 235 m on a side (the water having 11 mg O_2/L which is saturation at about 10° C. The volume of Lake Superior is 930,000 times greater than that. To put it

another way, if a year's worth of effluent from all nine mills could be magically saved up, simultaneously dumped into Lake Superior and thoroughly mixed, the potential deoxygenation would be from 11 mg/L to 10.996 mg/L, essentially a non-detectable change.

We conclude that there is no reason to regulate for lower BODs in kraft mill effluent, as far as overall impact of deoxygenation on Lake Superior as a whole. Although it is a fragile body of water it has enormous dilution capacity. Therefore we have rejected the so-called Best Available Technology (BAT) approach of MISA because of the commonly assumed interpretation that it requires secondary waste treatment. We have recommended (Section 11) that BOD be controlled as necessary to maintain good concentrations of dissolved oxygen in the receiving waters at each particular mill-site(which conforms with the "water quality" approach of MISA).

As described in Section 8.6, some mills with lake outfalls do not have major effects on dissolved oxygen. At one mill with a good diffuser, no appreciable change of oxygen concentration could be detected (Craig et al. 1986). A neighbouring mill without a diffuser caused oxygen levels of 3 to 5 mg/L inshore, in a bay, with reduced concentrations of oxygen over an area of about 1 square kilometre (Flood et al. 1986). That is undesirable but it is not a major catastrophe.

There are at least two more severe problems of unsatisfactory dissolved oxygen caused by Ontario kraft mills. Concentrations in the Wabigoon River were as low as 2.3 mg/L in the summer of 1984 (Beak 1985), far lower than our Low Level of Protection, and close to concentrations that would be lethal to fish. Those conditions prevailed although the effluent from the aerated lagoon was the second best of the 9 Ontario kraft mills. There was some effect from decomposing deposits in the river from previous years. Obviously those oxygen concentrations were not satisfactory.

A second unsatisfactory situation exists in the Kaministiquia River at Thunder Bay, in a location that should not be regarded as a river, but as an inlet of Lake Superior. This is the most massive discharge of BOD among the 9 mills (43 tonnes per day), and oscillations of the lake can carry the waste upstream or back and forth, creating awful conditions of dissolved oxygen of 1 mg/L and less (Klose 1987). The situation is complicated by varying priorities for flow regulation at an upstream dam, and plans for a major fish culture operation which would require young salmonids to run the gauntlet of the mill's effluent barrier, in order to reach Lake Superior.

We were much disturbed by the remedial plans that were underway at the time of our visit to the Thunder Bay mill, in the summer of 1987. Those plans were for oxygenation of the river to relieve the desperate situation of low dissolved oxygen. We regard that as a completely unsatisfactory "band-aid" approach which would lead to years of experimentation, increasing complexity of apparatus and cost, and continued dismal prospects for aquatic organisms.[3] We recommend either state-of-the-art secondary treatment, or relocation of the outfall, or both.

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3 We understand from more recent information that this idea has been abandoned.

6.3.3 Nutrients

SUMMARY. Kraft mills contribute 65% of the phosphorus from industrial sources that reaches Lake Superior, and they are about one-third as important as municipal waste treatment plants. It is desirable but not urgent, to reduce phosphorus inputs to the lake, to maintain its oligotrophic status. Thunder Bay itself is enriched and has higher algal growth than anywhere else in the lake. Continued progress with in-plant control of losses will reduce discharge of phosphorus as well as other things. Use of phosphoric acid and other cleaning agents containing phosphorus should cease.

By nutrients we mean minerals that are essential for nutrition of algae and other organisms. Nutrient discharges are closely related to BOD since they are released by the breakdown of organic matter. Secondary waste treatment is of little benefit in reducing the outputs of nutrients; by decomposing organic matter it makes the nutrients more immediately available in the receiving water.

Phosphorous is the key nutrient in almost all fresh waters and algal production is in almost direct proportion to the amount available. If phosphorus is supplied, there is usually enough of the other nutrients already present, to support algal growth. Again we were most concerned about Lake Superior as a site of potential enrichment or eutrophication, because this is an oligotrophic or clear, low-nutrient lake..

Phosphorus (P) measurements are available for the four kraft mills that discharge directly or nearly directly to Lake Superior (MOE 1987). All four were within the limits allowed by the Ministry. The 1986 average amounts per day and amounts per tonne of product are listed in Table 6.5, with the bottom row representing an unbleached mill.

Table 6.5 Phosphorus discharges from four Ontario kraft mills.

kg P/day	tonnes P/year	g P/tonne ADt/pulp
131	45.2	63.1
76.4	26.4	71.0
30.3	10.4	69.7
18.7	6.45	25.6

Thus the 4 mills contributed 256 kg/d or 88.5 tonnes/yr of P, assuming an operating year of 345 days. That is not a major contribution to the phosphorus loading of Lake Superior, which as of 1976 was receiving 4,200 tonnes per year (PLUARG 1978). The 88 tonnes is significant, however, compared to the total industrial loading of 135, and municipal sewage treatment plant contributions of 268. Those are the controllable sources, and to maintain oligotrophy in Lake Superior, the total loading should be reduced by 200 tonnes/yr (PLUARG 1978). (There is little chance of reducing atmospheric input of 1,570 and diffuse input via tributaries of 2,220 tonnes).

Thunder Bay (the body of water) is the only part of Lake Superior that is considered to be enriched to the status of mesotrophic (PLUARG 1978). (Some parts of the US shoreline are part way between oligotrophic

and mesotrophic.) The municipality of Thunder Bay produces 121 tonnes of P per year but most of that is removed by tertiary treatment, and only 31 t/yr reach the bay (Romanick 1987). Thus the city's contribution is somewhat lower than the 45 tonnes from the kraft mill. There are also non-kraft mills discharging to Thunder Bay.

Phosphorus from mills is thus an appreciable but not dominant portion of the man-made direct discharge of P to Lake Superior. We are not recommending any major control effort, but this report gives heavy emphasis on controlling pollution by tightening up processes within mills, or modifying them to reduce losses. Such improvements should reduce P loadings as well as other things.

It is often considered that secondary waste treatment of mill effluent requires the addition of nutrients, particularly phosphorus, to make it work. That is only true if very high performance standards are required of the lagoon. It would be undesirable to go in that direction, from the point of view of nutrient addition to ecosystems. The lagoons at Espanola do not use added nutrients. High rate biological treatment systems, such as activated sludge, require much higher phosphorus additions, and that is one more reason why activated sludge is less desirable than a lagoon..

As a final point about nutrients, there should not be any unnecessary use of phosphorus compounds in the mill, such as phosphoric acid for cleaning. Alternative substances are routinely used in some mills and should be used in all mills.

6.3.4 Toxic Substances

The acute lethality of Ontario kraft mill effluents is discussed in Section 8.1, and toxic substances are given extensive coverage in several chapters.

Here, we will simply repeat that as of 1985 and 1986, only one of the nine mills was consistently non-lethal to fish, while two others were sometimes non-lethal. It has been 16 to 17 years since federal regulations and guidelines introduced the fish toxicity test (EPS 1971, 1972). The federal regulations have been one of the bases used in establishing provincial control orders. We think it is time that all mills were considered in the category of "new mills", and met the federal requirements for toxicity as they were established for mill practices that prevailed in 1971-72.

Reduction in amounts of chlorinated organic substances is one of the major thrusts of this report. The current estimated levels are shown in Figure 6.3.

Our estimates show that the lowest TOX output is much less than 1.0 kg/t pulp for a mill with a very small bleaching operation. For bleached kraft mills, the lowest value is 3 kg/t, for a mill with oxygen delignification, 50% hardwood furnish, and a biological treatment system. The highest output of TOX is three times as high, at 10 kg/t for a mill bleaching 100% softwood by traditional bleaching procedures and without secondary effluent treatment. The nine mills are apparently contributing 33 tonnes per day of organochlorine to the environment. We feel that these are high numbers, considering that this class of substances contains many dangerous persistent toxicants, and that only a very small percentage of the organochlorines in mill waste have been identified.

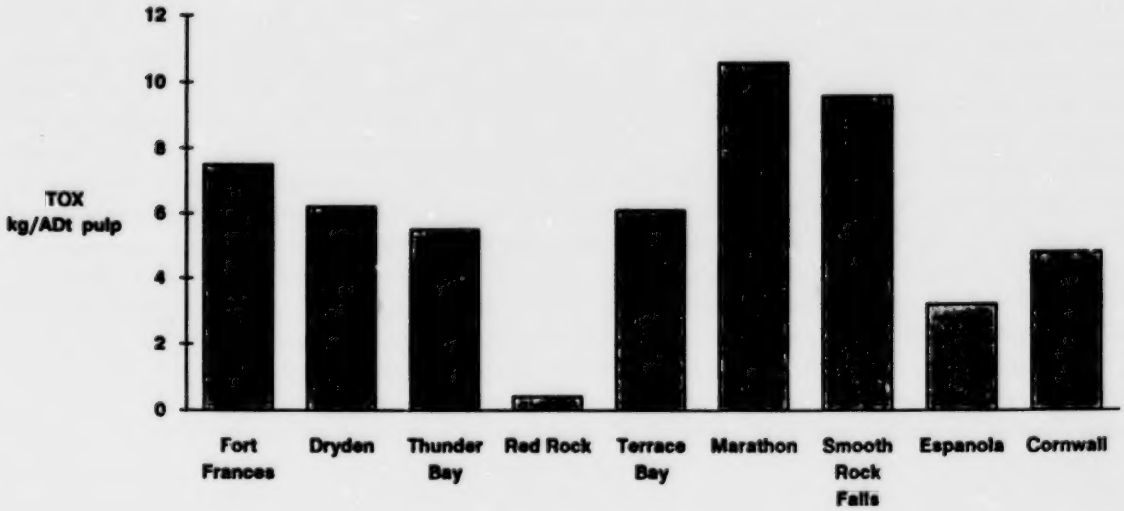

Figure 6.3 Estimated organochlorine discharges from Ontario mills. (Calculated from 1987/1988 mill operating data, using Germgård's equation from Section 9.8, assuming 33% removal in aerated lagoons, where they exist [4])

6.4 Effluent Quality in Mills Located Outside Ontario

SUMMARY. Kraft pulp mills in the US are more stringently regulated than are mills in Ontario. All but 2 US kraft mills have secondary treatment facilities whereas only 3 Ontario mills have such systems. The average emission of BOD from Ontario mills is over 4 times higher per tonne of output than the US average while suspended solids discharges are approximately equal. Only two Ontario mills would meet US regulations on BOD and TSS. In Sweden regulatory effort has shifted from controlling BOD levels in mill effluent to controlling the discharge of organochlorines.

6.4.1 Effluent Quality and Regulations for "Conventional" Pollutants in the US

New source performance standards and pretreatment standards from existing and new sources in the pulp, paper and paperboard industry were promulgated in November 1982 (US 47 FR 52006, 1982). The regulations contained in that document rest on the application of what is termed the best practical control technology currently available (BPT). The U.S Environmental Protection Agency (EPA) has set BOD and TSS limits for 33 sub-categories in the pulp and paper industry. BPT-based regulations for the bleached market kraft sector allow a maximum discharge rate for BOD and TSS equal to 5.5 kg (BOD) and 9.5 kg (TSS) per tonne of output. Limits for the unbleached kraft and semi-mechanical sector have been set at 2.1 kg for BOD and 3.8 kg of TSS per tonne of output.

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[4] The value for the Red Rock mill is exceptionally low because only about 10% of the kraft pulp is bleached

For conventional pollutants (BOD and TSS), the 1977 amendment to the US Clean Water Act established best conventional pollutant control technology (BCT) as the guideline to be applied to effluent from pulp and paper mills. The Environmental Protection Agency's regulations designed to specify BCT based restrictions were challenged in court by the American Paper Institute in 1981, the court required EPA to establish a two-part test with which to judge the reasonableness on economic grounds of the proposed BCT regulations: a Publically Owned Treatment Works (POTW) cost comparison test and an industry cost effectiveness test. The former test requires that the cost per pound of conventional pollutants removed when upgrading from BPT to a BCT candidate technology must be less than the cost per pound of conventional pollutants removed in upgrading a publically owned treatment works from secondary treatment to advanced secondary treatment. For the pulp and paper industry the POTW benchmark (in 1978 first quarter dollars) is $0.28 Us per pound. The industry "cost effectiveness test" involves computing a ratio which rests on a comparison of incremental costs per pound of pollutants removed by BCT technology relative to BPT technology. The ratio is then compared to a benchmark based on POTW data. If the industry ratio is lower than the benchmark, the BCT candidate technology passes the test. It is immediately apparent that both tests are somewhat bizarre both from the viewpoint of environmental protection and from economic efficiency. None of the candidate technologies initially proposed by the EPA passed the two part test and in consequence BCT has been set equal to BPT. (Details of the candidate technologies and revised effluent quality limitations for conventional pollutants from existing sources is given in 51 FR45232 Dec. 17,1986).

At this time, most Ontario mills would have very considerable difficulty in meeting EPA requirements for discharge of the "conventional" pollutants, BOD and TSS. Actual discharges from US kraft pulp mills are, with few exceptions, considerably below those presently experienced in Ontario. A review of data on BOD and TSS emissions from US mills for 1984 indicates that the average emission of BOD is equal to 3.68 kg per tonne of output. (We have attempted to include in our coverage of US mills those facilities that are similar to Ontario mills in terms of both size and type of products produced). By contrast, the average in Ontario, based on data for 1986, is equal to approximately 17 kg per tonne of output. It should be noted that two Ontario mills have BOD levels which would place them at the low end of the range of US dischargers: Espanola with a BOD discharge of 2.5 kg/t and Dryden with 2.6 kg/t of output. The Fort Frances mill with a BOD level of 9.2 kg/t would place in the upper range of US dischargers. All other Ontario kraft mills have BOD levels which significantly exceed those for US mills.

The very large difference in BOD discharges between US and Ontario mills is due to the fact that all US mills have secondary waste treatment systems. By contrast only Espanola, Dryden and Fort Frances mills have such systems in Ontario.

With respect to TSS levels, the average discharge from US kraft pulp mills was equal to 6.3 kg per tonne of output. (It should be noted that two mills in the sample were not in compliance with EPA TSS limits. If those are removed from our sample, the average falls to under 5 kg per tonne of output.) The average discharge for Ontario mills is very similar, at 6.5 kg of TSS per tonne of output. Table 6.6 provides a comparison of Ontario and US EPA limits as would apply if the EPA standard was adopted in Ontario. We have computed EPA limits for Ontario mills on the basis of "new" as opposed to "existing" point source standards. In fact, mills at Cornwall and Smooth Rock Falls would be classified by EPA as "existing" discharges and would have higher limits than those estimated in Table 6.6. MOE (1987) contains a similar exercise for the entire Ontario Pulp and Paper industry. Our analysis is independent of the MOE analysis and in a number of cases achieves results that are slightly different. This is simply due to the difficulty of attempting to decide which specific sub-category a given production block should be placed in . If a mill is discharging into a sensitive water body, the US limits would be considerably lower than those given in the

Table 6.6. The table does, however, serve to indicate the large differences in effluent quality across mills in Ontario and the generally tighter limitations on mills imposed in the US when judged against the traditional criteria of BOD and TSS.

Table 6.6 Comparison of US EPA and Ontario effluent discharge regulations for "traditional pollutants", applied to Ontario mills.

Mill location	BOD tonnes/day			Suspended Solids tonnes/day		
	Ontario.	EPA	Actual	Ontario.	EPA	Actual
Fort Frances*	15	3.8	10.5	7.5	6.5	4.5
Dryden*	-	4.0	2.6	5.6	6.6	3.3
Thunder Bay	55	11.5	43.1	14.0	19.7	13.7
Red Rock	23	1.8	17.2	5.5	2.7	4.0
Terrace Bay	42.7	5.9	29.6	8.5	10.4	5.4
Marathon	15	2.6	14.3	6	3.0	2.9
Espanola*	3.6	5.5	2.2	-	9.4	5.1
Smooth Rock Falls	9	1.7	7.0	4.5	3.0	2.9
Cornwall	27.7	1.9	15.1	-	2.6	7.9

* *indicates that secondary treatment is in place. - indicates that limits are not defined.*

At this time, the US EPA does not regulate organochlorine discharges. However, the EPA is in the process of reviewing its regulations in the light of work being carried out on the presence of persistence toxic substances in pulp mill effluent.

6.4.2 Regulation of Toxicity in the US

SUMMARY. (1) The US EPA rediscovered effluent toxicity testing in the early 1980s. (2) Such toxicity tests are now incorporated into US waste discharge permits, along with the previous approaches using water quality criteria for individual chemicals, and "Best Available Technology". Biological surveys in the receiving water are also utilised. (3) Toxicity is tested with a fish, an invertebrate, and an alga, generally fathead minnows, the waterflea Ceriodaphnia, *and* Selenastrum. *The most sensitive species is used to judge toxicity. (4) The toxicity regulations generally require that peak concentrations should not cause lethality outside a mixing zone. Sometimes they require that full-strength effluent should not have lethal effects. (5) It is also required that there be no sublethal effects on growth and reproduction, at the average concentration expected at the edge of a mixing zone. (6) The effluent toxicity regulations are achieving some success, for example most of the pulp and paper mills in Wisconsin now meet them. (7) The entire US approach is overly complex and has some blind spots for control of kraft mill waste, but Ontario's approach would benefit by adopting tests with several kinds of organisms, especially at sublethal levels.*

The water quality criteria approach of the 1970s

Starting in the late 1960s, continuing through the 1970s and into the early 1980s, the United States had a fairly single-minded approach to controlling toxic water pollutants. Efforts were devoted to collecting information from toxicity tests, and producing numerical values for "safe" concentrations of the various toxic chemicals. Pollution was then to be controlled by regulating the amounts that could be discharged, without exceeding the desired concentration in aquatic ecosystems. Monitoring would involve chemical measurement of actual concentrations in effluent and/or the receiving water. For toxicants, this approach received much more attention than "best-technology"avenues.

A great deal of scientific, technical, and administrative time went into development of these water quality criteria and water quality standards. From this approach, and as part of the outcome of the Clean Water Act mentioned above (Section 6.4.1), there eventually arose the famous list of 129 "priority pollutants". **A major problem with this approach was concern for those chemicals, but frequent total neglect of pollutants that were not on the list, but were important in some situations.** One glaring example of this blind spot applied to the pulp industry. Certain chlorophenolics are on the list (PCP and TCP). If a mill certified that it did not use such compounds, then it was not required that they be monitored. **The idea that large tonnages of chlorinated organics would be manufactured in the bleach plant was ignored, because the generic category was not on the list of priority pollutants.** There are similar oversights in lists of chemicals to be considered by MISA.

A complex set of rules was set up to specify the types, numbers, and quality of toxicity tests that were required before a water quality criterion could be estimated (Stephan et al. 1985). For example 8 organisms from specified groups or families had to be tested. For each substance, a specified maximum concentration was not to be exceeded more than once in three years (actually considered a maximum one-hour average), and that maximum was estimated to protect 95% of the species in a community against lethal effects. There was also a considerably lower concentration to protect 95% of the species against chronic effects; it was considered to represent a four-day average that was not to be exceeded more than once in three years.

US effluent testing; reinventing a wheel and improving it

Throughout this "water quality" era, some toxicity testing of effluents was carried out by governments, although such tests were not part of official requirements. For example there were 74 toxicity tests on 10 paper industry effluents in Florida during 1978 to 1985, carried out by EPA and the Florida state agency, i.e. almost one per mill per year.

Nevertheless, the main administration of EPA appeared to be blissfully unaware at the time, that toxicity tests were being used on effluents in other countries. In the 1980s it apparently dawned on the Washington office that there were approaches other than water quality criteria, and some statements since then have an air of naiveté. "The US Environmental Protection Agency (EPA) has found, through laboratory and field research, that biological testing is a scientifically valid approach to control toxic[ant]s in wastewater discharges" (Wall and Hanmer 1987). [We never thought that the issue was in doubt.] From the same article: "assessment and control of .... toxic discharges .... is often incomplete without the use of living organisms as indicators of toxic effects." [We regard "often" as an understatement, and have pointed out elsewhere that toxicity can **only** be measured by effects on living organisms.] "Because these techniques

or their application to effluent testing are new, ..." (EPA 1984). [New? .... regulations for toxicity tests on effluents have been in place since 1971, a little to the north in Canada, and the concept of effluent testing to detect toxic streams goes back much further, at least for example, to Bergström and Vallin (1937).]

EPA developed biotests vigorously, started using them in a formal system of discharge permits, and in fact, now makes much heavier use of biological testing than is the case anywhere in Canada. Along with the toxicity tests, the previous "Water Quality Approach" is retained with its water quality criteria. The BAT[5] approach is still incorporated into the permits as described above (Section 6.4.1). Furthermore, biological surveys in the receiving water are often required by the permit. The combination can result in very restrictive limits for discharge. The current approach to toxic substances is outlined below, from information taken chiefly from Giattina and Anderson-Carnahan (1986) and EPA (1985).

The US Clean Water Act has a basic tenet that "the discharge of toxic pollutants in toxic amounts be prohibited", and has a goal of zero discharge of pollutants. Since that does not seem to be attainable at the moment, the Act allows for a system of permits to discharge certain kinds and amounts of things, specified on a case-by-case basis. This closely parallels the Canada Fisheries Act which prohibits the discharge of any deleterious substance, and the Control Orders of the Ministry, which specify allowable exceptions. In the U.S., the federal permit system is called "The National Pollutant Discharge Elimination System" or NPDES permits for short. Granting of permits is normally delegated to each state, but EPA retains a veto power and will take back the responsibility if it is not satisfied with the state standards. As of May 1987, there were 440 permits or applications for permits associated with the pulp and paper industry.

Of most interest to this report and the Ontario situation, are the relatively recent US procedures for testing effluents. The additional approach was announced (EPA 1984) as a way of complementing the deficiencies of previous chemical approaches, and going beyond BAT. The number and kind of toxicity tests vary considerably with the state, but EPA recommends the following.

(1) Tests of acute lethality

Three species are to be tested, a fish, an invertebrate, and a plant. Often these would be the fathead minnow, the waterflea *Ceriodaphnia* sp., and an alga.

The lethality test is used in somewhat different ways, depending on the regulations of different states. Each of the three cases below applies to the most sensitive of the three species for a particular effluent.

(a) The concentration of the effluent must not be more than 0.33 LC50, at the edge of a mixing zone. (For example, if there were 10-to-1 dilution available, the LC50 of the effluent should not be greater than 33% effluent; diluted it would thus be one-third or less of the LC50.) This approach prevails in most of the states and is used in permits.

(b) The effluent LC50 is to be > 100%. This is specified in some permits, with the intention that even within the mixing zone there will not be acute lethality.

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5 *BAT: "Best Available Technology"*

(c) The effluent LC1 is to be > 100%, i.e. full-strength effluent should not cause more than 1% mortality. EPA considers this to mean that the acute lethality of the whole effluent would not be greater than 0.33 of the LC50. In truth, one cannot determine precisely whether the LC1 is greater than 100%, in any test with realistic numbers of organisms. In practice it usually is taken to mean less than 10% mortality in 100% effluent. We have not seen this third version applied in any permits.

If there is an efficient diffuser with high escape velocity of effluent, requirement (b) would not apply at the end of the pipe, but at the edge of a small discharge zone.

(2) Sublethal tests

Three species are to be tested. Ordinarily the tests would be: (a) the 7-day growth and survival test with newly-hatched fathead minnows; (b) the 7-day *Ceriodaphnia* test for survival and number of young produced; and (c) growth during 4 days of an alga (*Selenastrum capricornutum*).

The no-observed-effect concentration (NOEC), in tests with the effluent, is to be higher than the concentration which will prevail after complete mixing, i.e. there should be no sublethal effects at the edge of a designated mixing zone.

For discharge to a river, the requirement must be satisfied at low flow, normally taken as the 10-year minimum value for 7-day average flow (the 7Q10).

(3) Frequency

The tests of acute lethality with three species would be performed:

(a) on four separate samples collected during 24 hours;

(b) once a month for the first year of the permit; and

(c) twice a year thereafter.

(That would be 144 acute toxicity tests during the first year. However, after 2 months only the most sensitive species need be continued, thus 64 in the first year. Also there could be a stipulation to cease testing if all results were > 100% for the first two months (EPA 1985)

The sublethal tests on three species would be done once a month for the first year, and twice a year thereafter.

We have simplified the above description and omitted some of the more complex or arbitrary rules. In practice, the calculations are made in terms of toxic units (lethal and sublethal toxic units) since that makes it easier to comprehend and to do the arithmetic. These effluent toxicity values would be applied in similar fashion to the water quality criteria, i.e. a maximum one-hour peak and a maximum 4-day average as described at the end of Section 6.4.2.1.

Are the US toxicity requirements enforced?

The brief answer to the question is yes. Effluent toxicity tests have been consistently included in pulp mill permits for the last two or three years, the program appears to be taken seriously, most mills around the Great Lakes meet at least the lethality requirement (personal communication, L. Anderson-Carnahan, EPA Duluth), and most Wisconsin mills meet the sublethal tests (Kraus and Kornder 1987).

If the toxicity requirements are not met, there can be fines but typically the industry is required to discover the cause of the toxicity and reduce or eliminate it. EPA has a formal procedure for this which it calls "Toxicity Reduction Evaluation" (Anderson-Carnahan and Mount 1987). A series of ingenious and short-cut tests are carried out, in an attempt to identify the general category of chemical(s) causing the problem.

We have copies of some NPDES permits for pulp and paper mills, and requirements vary with state or EPA district and apparently with the particular site. Requirements are also changing over recent years.

A permit issued in Georgia in 1985 stipulated that full-strength effluent should not be lethal to more than 50% of an appropriate fish and invertebrate. The test-schedule was as given above except that it started at 3-month intervals.

A permit for a mill in Idaho in 1985 required determination of the no-effect level in 7-day life-cycle tests with *Ceriodaphnia* sp., every 3 months. Results were to comply with the requirement for no sublethal effects outside the mixing zone.

Permits for two mills discharging to the Pacific in California were issued in 1987 following extensive environmental studies. Each mill was required to carry out a lethality test with shrimp every month, a chronic test with mussels monthly, and chronic tests with two other species on a quarterly basis. The mills also had to carry out weekly measurements of BOD, TSS, settleable solids, DO, ammonia, 16 resin and fatty acids, two guaiacols, and 3 chlorinated resin acids. Quarterly measurements (a few monthly) were oil and grease, 10 metals, 9 pesticides and phenolics, and 2,3,7,8-TCDD. Finally there were quarterly chemical surveys at 17 stations in the receiving water, annual biological survey at 13 stations, as well as fish population studies, *in situ* mussel toxicity, sediment analysis, and bioaccumulation assessment!

An example that EPA means business comes from Wisconsin. In 1986, all the mills in the state came up for renewal of NPDES permits. The state proceeded to do that but EPA vetoed all eleven permits because "they do not require specific limits on the toxic chemicals, limits on the overall toxicity of the discharges, or sufficient discharge monitoring" (Press release, EPA Region 5, Chicago, December 3, 1986). Wisconsin responded with effluent tests, and a recent revision (January 12, 1988) includes the following requirements.

> LC50 > 100% effluent, for month-old fathead minnows, newly-released *Daphnia magna*, and one other species.
>
> No effect in the 7-day growth test with newly-hatched fathead minnows, or on the number of young produced by Ceriodaphnia, at the concentrations expected at the edge of the mixing zone.
>
> The tests to be done once every three months during the first year, and once a year thereafter.

Comments on the US effluent toxicity program

One major comment on the above program is that it is admirable in its scope for protecting aquatic ecosystems from toxic substances in effluents. In particular, testing three different types of organisms is protective, since there are major differences in relative sensitivity to various kinds of effluents. Addition of a non-algal micro-organism to the battery of tests might be even more revealing since they are often most sensitive (Sloof et al. 1983).

The program is also extremely complex and would appear to consume a mind-boggling amount of time of technical people, simply to understand and implement the procedures. For example the "Technical Support Document" that is intended to explain the approaches (EPA 1985) has some 106 pages of small print and intricate detail. A training manual for permit writers has 165 pages of single-spaced typing (EPA 1986).

The direct costs of the effluent toxicity tests for a typical mill can be estimated as follows. Using recent commercial costs in Toronto, the first year of testing on the schedule recommended by EPA (preceding items (1) to (3)) would cost about $ 21,000 for the lethality tests and $ 27,000 for the sublethal tests, thus almost $50,000 plus collecting, shipping, and reporting. The real cost to mills, including staff time would probably exceed $100,000. For the much more extensive testing required for the California mills the total cost will be left to the reader's imagination.

The paper industry has criticised the sublethal tests, particularly the one with *Ceriodaphnia* sp., as being variable, unreliable, and unacceptable as a regulatory tool. The chief problems were difficulty in culturing and having organisms available at the right time, poor performance of controls, difficulty in weighing small fish with accuracy, and the expense of large amounts of labour (Kraus and Kornder 1987). There is some truth in those claims.

We do not suggest slavishly following the US approach. In many respects we feel it is too complex, and can require monitoring far too many items, resulting in a poor ratio of effort to payoff in control of important pollutants. There is advantage, however, in adding biological tests with organisms other than fish, particularly at the sublethal level, and we are recommending those things for Ontario.

6.4.3 Effluents and Discharge Fees in Federal Republic of Germany

The current regulations on pulp mills in west Germany do not seem to be particularly strict, and the limit for BOD seems high. This is probably because west Germany has sulphite mills, not kraft mills. However, stricter regulations are coming in 1989. There are already regulations which impose fees for units of waste discharged, and these would appear to be remarkably large.

The nineteenth General Administrative Regulation under the Federal Water Act lists the minimum requirements for pulp and paper effluents. We have attempted to apply them to James River Marathon, which is median for Ontario kraft mills for BOD, and is relatively small in its daily production of 435 tonnes of bleached kraft pulp.

These current German regulations would allow a maximum water use of 200 m^3/t, which is 1.35 times the actual use at Marathon. Suspended solids limit is 10 kg/t or 4.35 tonnes per day, 1.5 times the actual discharge at Marathon. The Ontario control order would, however, allow twice as much suspended solids as the German regulation.

The present German BOD limit is 70 kg/t for bleached pulp mills, thus 30 t/d for Marathon, twice the actual discharge. The German limit is more than 11 times the allowance that would apply under US EPA regulations. However, the average BOD at German mills is less than half the allowed amount (Huber and Baumung 1987), no doubt because of the fees charged by government (see below).

Toxicity regulations would require the LC50 to be equal to or greater than 12.5% which is much less strict than Canadian or Ontario rules. In 1986 the median LC50 for Ontario kraft mills was >28%, which would pass the German requirement.

New regulations proposed for 1989 are much more strict. The BOD allowance for "bleached paper pulp" may decrease to 10 kg/t (instead of 70), and fish toxicity may change by a factor of 4, to an LC50 of 50% effluent. Furthermore there may be a maximum allowance for organic chlorine of 1 kg AOX/t of bleached pulp. However, the industry feels that those values are overly strict and they may be relaxed slightly (Huber and Baumung 1987). Five of the eleven mills already use oxygen or peroxide bleaching.

Another aspect of the German regulations already appears to be strict compared to the Ontario situation. There are fees charged by the government in relation to the amounts of pollutants discharged, under the Waste Water Charges Act passed in September 1976. If we interpret the terms correctly, and we have a version of the Act written in English, a small Ontario mill might pay a million dollars a year if the fees applied here.

Most of this would be for toxicity, if our calculations are correct. The German regulation stipulates that "one unit of noxiousness" for toxicity to a certain fish, equals 0.3 times toxic units of the effluent for a volume of 1000 m^3. Toxic units may be calculated as 100/LC50 in %. The fee structure is accordingly based on Toxicity Emission Rate (see Section 8.8). If we take our median Ontario LC50 of 28%, and the flow of a smaller mill like Marathon, the calculation would be as follows.

$$0.3\ (100/28)\ (64{,}000/1000 \times 365) = 25{,}000 \text{ units.}$$

Each unit attracted a fee of 40 Deutschmarks in 1986, thus almost a million Dm or approximately 740,000 Canadian dollars at early 1988 rate of exchange.

The German fee for solids is based on settling solids, and one unit would be one cubic metre or one tonne. If we assume those are suspended solids, a mill like Marathon with 1060 t/y would pay fees of $31,000. COD is used to regulate in Germany, and 100 kg represents 2.2 units of "noxiousness". If we assume that BOD is only one-third of COD, Marathon's annual loading of 15,000 tonnes would rate a fee of almost a quarter of a million dollars.

The total current fee would apparently be slightly over a million dollars a year, an appreciable sum. However, there is a provision in the German regulations that if the requirements for maximum discharges are met, there is a 50% reduction in fees. Thus in our example, the small mill would pay fees of half a million dollars.

It is further proposed to initiate a fee for organochlorines in 1989, of 20 Dm per tonne of AOX, or about $14.75. For a mill like Marathon, with an estimated output of almost 5 t/day TOX, that might translate to $25,000 per year.

There is a very substantial literature on the determination of the optimal price (or tax) to be charged per unit of pollution. Although determination of the theoretically "correct" price is not difficult, setting the "actual"

price is fraught with a number of very difficult problems. It is also interesting to note that an increase in an industry wide effluent charge may lead to individual firms increasing the amount of pollution (Endred 1983). Furthermore, de Meza (1985) notes that an increase in the tax levied on a unit of pollution may have the perverse effect of increasing environmental damage.

In the above discussion, we are sure of the maximum limits, but not of the interpretation, calculation, and application of the fees since we have not visited Germany or talked directly with anybody with first hand experience.

6.4.4 Effluent Quality and Regulations in Scandinavia

An analysis of regulations governing the quality of pulp mill effluent in Finland and Sweden provides an interesting contrast in regulatory philosophies. In both countries the pulp and paper industry is a major source of income and employment. Although the Swedish pulp sector is larger than the corresponding Finnish sector (Sweden produced 8.9 million tonnes in 1984 compared with 7.7 million tonnes produced in Finland), the Finnish sector is more important in terms of its impact on the national economy.

From the mid-1950's to the latter part of the 1970's the regulatory emphasis in both countries was on reducing the discharge of oxygen-consuming biologically degradable substances and fibres. Over the period 1955 - 1985, the average specific emission of BOD_7 was reduced by close to 90% (measured in terms of kg of BOD_7 per tonne of output) with the largest reductions coming from the unbleached pulp lines (SSVL-85 1985, Committee for the Gulf of Bothnia 1987). Although regulation of emissions was very similar in the early 1970's in both Sweden and Finland, regulatory approaches to pulp mill discharges in the mid-1980's have diverged considerably.

In recent years, Sweden has placed great emphasis on reducing the emission of total organically bound chlorine as opposed to achieving a further decline in BOD, whereas the Finns seem more concerned about BOD. In this context it should be noted that most Swedish mills discharge into the Baltic Sea and in consequence dilution of BOD is adequate. The rationale for controlling organochlorine discharges is detailed in Section 9.

We have obtained detailed emission data for all Swedish and Finnish pulp and paper mills together with data on the type of internal and external pollution control measures in force in each mill. (The data cover 141 mills). In order to highlight the major improvements that have occurred in effluent quality from bleached sulphate mills in both countries since 1970, it is convenient to present a brief description of mill technology and pollution abatement procedures as they were in the early 1970's and contrast this with the current situation.

Summary data on effluent quality in Finnish and Swedish sulphate pulp mills are given in Table 6.8 for mills using softwood and hardwood furnishes. Both sets of data represent the "average" situation for Finnish and Swedish kraft mills.

The organochlorine discharges from Finnish mills are reported in Table 6.7. Notice that some mills with activated sludge treatment have relatively low discharges, but this ignores the problem of disposing of the significant quantities of waste sludge from these plants without releasing the organochlorines to the environment.

Table 6.7 Organochlorine discharges from Finnish mills.; Source: Ekström 1987, TOX values added by present authors

Mill	Market Pulp	TOCl kg/t pulp	TOX kg/t pulp	
Aanekoski	YES	1.4	1.8	Activated sludge, Extended delignification
Varkaus	NO	2.6	3.4	Aerated lagoon, Extended Delignification
Mantta	BOTH	2.6	3.4	Activated Sludge
Villmanstrand	YES	2.8	3.6	Aerated Lagoon
Kemi	YES	2.9	3.7	Hardwood pulp
Jakobstad	BOTH	2.9	3.8	Activated Sludge, mostly hardwood
Uleaboug	YES	3	3.9	Primary Treatment
Kasko	YES	3.5	4.6	Aerated Lagoon
Tainionkoski	BOTH	3.7	4.8	Primary Treatment
Kemijarvi	YES	3.8	5	Primary Treatment
Joutseno	YES	4.1	5.3	Activated Sludge
Kaukopaa	NO	4.4	5.7	Primary Treatment
Sunila	YES	4.6	6	Aerated Lagoon
Kuusanniemi	YES	4.8	6.2	Primary Treatment
Veitsiluoto	NO	5.1	6.6	Primary Treatment,
Uimaharju	YES	5.3	6.9	Primary Treatment
AVERAGE	—	4	5	

Table 6.8 Emissions from the production of bleached sulphate pulp. This is prior to external treatment (excluding wood room losses). Source: Committee for the Gulf of Bothnia (1987).

	BOD_7 kg/t	COD kg/t	SS kg/t	TOCl kg/t
Softwood				
1970 technology Finland & Sweden	55	190	15	>6
Current technology Finland	24	85	11	5
Current technology Sweden	19	65	8	3.5
Hardwood				
1970 technology Finland & Sweden	60	180	28	4
Current technology Finland	25	75	12	2.5
Current technology Sweden	25	75	9	2.5

6.4.5 Sulphate Technology in Finland and Sweden in 1970

Technology in 1970 was roughly the same in both countries. With respect to cooking operations in softwood pulping, the Kappa number for pulp to be bleached was 30-35 in Finland and approximately 35

in Sweden. For hardwood pulp, the respective Kappa numbers were 22-25 (Finland) and 18-20 (Sweden). The washing of pulp was not particularly efficient when compared with current technology. The chemical content of the liquor remaining in the pulp equalled 18-20 kg/tonne of easily removable Na_2SO_4. In plants with discontinuous cooking, washing occurred in diffusers or on 3-4 filter washers. In plants cooking in a continuous process, pulp washing was more efficient as the pulp was given a first wash in the lower part of the digester before progressing to a 1-2 filter washers. Most bleach plants were fitted with filters for the incoming pulp and the incoming washing loss in the bleach plant was roughly 5 kg Na_2SO_4 per tonne of softwood pulp (equal to 8 kg of COD per tonne).

The most common bleaching sequences in Sweden were CEHDED and CEHEDED. In Finland the typical sequence was CEHHDED. In the pre-bleaching stage, chlorine dioxide was not used. Condensate, with minor exceptions, was normally discharged in untreated form. This implies that some of the condensate was discharged along with the bleach plant effluents.

6.4.6 Current Sulphate Technology in Finland and Sweden

Kappa numbers have been reduced slightly in most plants since 1970 as a result of better cooking practices. For unbleached softwood pulp a representative plant would have a Kappa number of 30 in Finland compared with 32 in Sweden. The respective Kappa values for unbleached hardwood pulp are 20 and 18. Two mills in Finland and one in Sweden have adopted the practice of extended cooking. In the Finnish cases, unbleached pulp is cooked to a Kappa value of 25 for softwood and 15 for hardwood. In the Swedish mill, softwood pulp shows a Kappa value of 25. The rationale for extended cooking is simply that if the alkali concentration during cooking is more even and the lignin value lower toward the end of the cook, the viscosity of the pulp will be unaffected at the lower Kappa number. From an environmental standpoint this is important since emissions from the bleach plant are reduced in proportion to the reduction in the Kappa number. Achieving a lower Kappa number is not costless. Extended cooking requires investment in additional equipment such as liquor accumulators, heat exchangers and a larger chemical recovery system. In addition, extended cooking reduces the pulp yield, thus marginally increasing operating costs. This increase may, however, be offset by greater heat generation.

Greater investment in washing facilities, together with improved washing procedures, has resulted in a significant increase in washing efficiency. "Normal" washing loss measured in terms of easily removable Na_2SO_4 is between 8-12 kg per tonne of oxygen bleached or unbleached pulp. (The equivalent values expressed in terms of COD are 10-15 kg/tonne for softwood and 15-25 kg/tonne for hardwood.) In the manufacture of bleached pulp, an inefficient washing operation will cause a larger amount of organic matter to enter the bleach plant and thus to a larger amount of material being chlorinated. In consequence, higher washing losses lead to increases in the discharges of organochlorines.

Most screening plants in Finland and Sweden exhibit a high degree of "closeness", meaning that water losses occur only when rejected material is discarded. All of the dissolved material that is not washed away accompanies the pulp to the bleach plant. Thus compared with the "open" 1970 style screen plant, the amount of dissolved organic material entering the bleach plant with the pulp is approximately doubled. Closing a screening operation will not, by itself, lead to a significant reduction in pollution. In addition to closing the screening operation, improved washing efficiency is required together with a reduction in the quantity of water circulating.

The most dramatic reductions in the emission of TOCl have occurred in Sweden as a result of the introduction of oxygen bleaching of softwood pulp. Out of the 15 Swedish bleached sulphate mills, 9 have introduced an oxygen stage and two more will likely introduce oxygen bleaching in the very near future. It is probable that the introduction of government policies to reduce the level of TOCl in mill effluent will lead all Swedish sulphate mills to install an initial oxygen stage by the early 1990s. The Kappa number for oxygen bleached pulp typically ranges between 17-20. After the initial oxygen stage, the normal bleaching sequence is (C+D) EDED with the C stage containing 15% chlorine dioxide (measured as active chlorine). The first alkali stage at the majority of mills is reinforced with peroxide or oxygen. At Swedish mills without an initial oxygen stage, the standard sequence is (C+D) EHDED with the chlorine stage containing 5-10% chlorine dioxide. The combination of oxygen bleaching and high chlorine dioxide use in the chlorine stage leads to a significant reduction in TOCl. The Swedish Environmental Protection Board estimates that in mills using both oxygen bleaching and replacement of chlorine with chlorine dioxide, emission of TOCl is reduced significantly in softwood lines.

Hardwood pulp in Sweden is generally bleached in a (C+D) EDED sequence with fairly high replacement of chlorine with chlorine dioxide. Two mills have an oxygen stage, one of which uses 30% chlorine dioxide in the chlorine stage. Reductions in TOCl are reported to be of the order of 30-50% compared with the traditional bleaching sequence.

In Finland, the most common bleaching sequence is D/CEDED,with the alkali stages being reinforced with peroxide or oxygen. This reinforcement permits a reduction in the amount of total chlorine required. Chlorine dioxide in the C stage is between 10-20% in softwood lines and between 5-85% in hardwood lines. Finnish mills are installing intensive mixers at a steady rate, permitting reductions in the quantity of bleaching chemicals and thus slightly lowering emissions of organochlorines. Two mills in Finland employ displacement bleaching. Water consumption in these mills is reported to be very low at 15 m^3/tonne. Reductions in organochlorine emissions have occurred in Finnish mills, but on average discharges are considerably higher than in Sweden.

In 1987 all Swedish sulphate mills and the majority of Finnish mills were equipped with condensate stripping columns. A small number of Finnish mills clean the condensates biologically and a number of mills have not, as yet, installed condensate treatment facilities.

6.4.7 External Treatment of Effluent in Finland and Sweden

Although the number of biological treatment plants has increased in recent years, not all Swedish and Finnish sulphate mills have biological treatment facilities. For example, of the 9 Swedish mills which use oxygen bleaching, only 5 have a biological treatment stage. A small proportion of the mills using a non-oxygen sequence or an extended cook have not, as yet, installed biological treatment phases.

In Sweden, the most common method of providing biological treatment of the effluent from sulphate bleach plants is by way of an aerated lagoon. A typical aerated lagoon will reduce BOD levels from the sulphate mill by between 40-90% and sometimes virtually eliminate acute lethality to fish. The efficiency in terms of reducing organochlorine discharges is lower. TOCl reductions in the range of 10-30% are generally considered to be normal according to Norström (1987).[e]

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e The present authors are more optimistic, as discussed in Section 5

In recent years there has been a large increase in the number of activated sludge systems in operation at pulp and paper mills, especially in Finland. By mid-1987, 8 Finnish plants had installed activated sludge systems with 5 others under construction. In Sweden, 3 systems were operational and 3 more were in the construction phase. Theoretically, and in the laboratory, the activated sludge process will attain reductions of between 80-95% in BOD and between 30-50% in organochlorines. Thus the process is technically more efficient than an aerated lagoon [7] (the technical problems associated with operating an activated sludge treatment system are discussed in Section 5). A major problem in the use of the activated sludge method is the large volume of sludge that has to be disposed of after dewatering. Finnish and also Swedish authorities report that this is now a significant problem for the industry.

6.4.8 The Cost of Secondary Treatment

Although external biological treatment is very efficient in removing BOD and also leads to some reduction in organochlorine levels, it is relatively expensive to install and operate in Finland and Sweden. Primary treatment itself (mechanical sedimentation), which is a necessary phase prior to biological treatment, has a capital cost of between 17-28 million SEK for a 300,000 tonne a year sulphate mill. Operating costs range between 0-8 SEK per tonne of pulp, depending on the amount of energy that can be obtained from the resulting sludge. The capital cost of constructing an aerated lagoon is reported to be about 70 million SEK (based on a 300,000 tonne a year sulphate mill with a BOD level of 24 kg per tonne of output and water use at 60 m^3 per air dried tonne). Operating costs are equal to 21 SEK per tonne of finished product. At current exchange rates, operating costs are roughly equal to $5 per tonne and capital costs to slightly under $15 million (Committee for the Gulf of Bothnia 1987). Information obtained from Canadian mills using aerated lagoons suggest that Swedish costs are in excess of those experienced in Canada. Operating costs are generally equal to $2.5 per tonne of output in Canada. Although capital costs are very mill-specific, we are aware of facilities that have been constructed for well under $15 million.

Capital costs for installing activated sludge treatment plants in Sweden have averaged around 100 million SEK (around $22 million). Operating costs are fairly high at 38 SEK (approximately $8) per tonne of finished product.

6.4.9 Recent Developments in Sweden

The National Swedish Environmental Protection Board was commissioned by the Swedish government in August 1986 to provide an action plan for the reduction of marine pollution. The Board published its recommendations in May 1987. Whilst noting that the pulp and paper industry had significantly improved effluent quality, the Board stated that the industry was the largest discharger of stable chlorinated organic materials and that it was technically and economically possible to further reduce the discharge of chlorinated organics from bleached sulphate mills to 1.5 kg of TOCl per tonne of finished product by a combination of oxygen bleaching and increased substitution of chlorine dioxide for chlorine. The Swedish government has accepted that emissions of TOCl per tonne of sulphate pulp be reduced to 1.5 kg/t[8] by

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7 In practice the activated sludge process is often less efficient than aerated lagoons in kraft mills, due to the variability of the raw effluent.

8 The data on organochlorines is defined in terms of TOCl, in accordance with the Swedish practice, whereas most of the data on organochlorines in this report is expressed as Total Organic Halogen, (TOX). TOX values are normally 30% higher than TOCl values, so that the Swedish limit of 1.5 kg/t pulp is equivalent to 2 kg/t TOX.

1992. The Swedish government has affirmed the above regulation in a number of operating permits by requiring that a number of kraft mills reach the 1.5 kg/t TOCl limits by 1989. Figure 6.4 shows that there already has been a remarkable decrease in chlorine use in Sweden.

It is recognised by both Government and industry that moving to a 1.5 kg/t TOCl level is not cost-free. Whilst there is agreement that introducing oxygen bleaching is both economically and environmentally beneficial (industry members opined that the so-called pay-back period was longer than that given by government officials), the additional steps required to reduce TOCl to 1.5 kg/t will clearly lead to an increase in the cost of production. At existing Swedish price levels, the cost for increasing the amount of chlorine dioxide to a level sufficient to achieve the required TOCl reduction is estimated to be 15 SEK (approximately $3 per tonne of pulp). Capital costs are estimated to be in the range of 25-40 million SEK ($5.5 - 8.8 million).

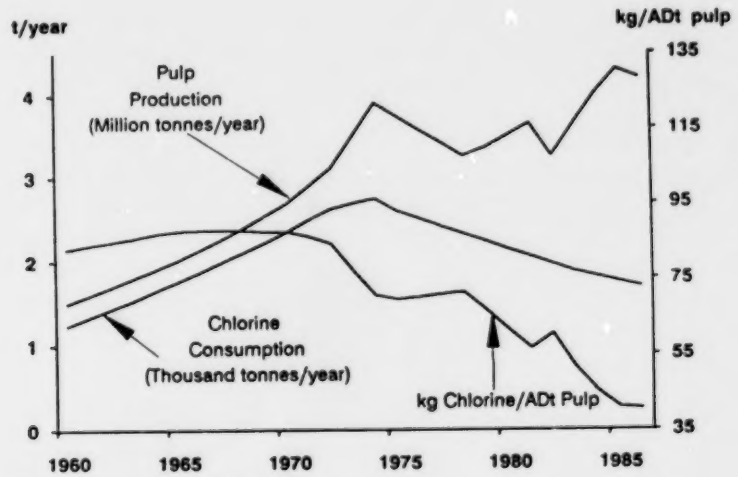

Figure 6.4 Chlorine consumption by Swedish kraft industry.

It must be clearly understood that the 1.5 kg limit is an intermediate target. The action plan states that "...(given) the risks presented by stable organic environmental toxins, it must be stated that the above limitations are insufficient. Accounting for the size and properties of the pulp industry discharge, there is no other long-term solution than the entire elimination of stable organic substances from these effluents". The long-term objective is to reduce the emission of TOCl to close to zero within a 15-20 year period. It is recognised that this will require considerable expenditures on research into pulping and secondary treatment techniques and will lead to a further increase in the production cost of pulp. It is clearly not possible to provide an accurate estimate of the cost of reducing TOCl emissions to a level close to zero since the optimal technology is largely uncertain. The Swedish government estimates that the capital cost of "essentially eliminating the discharge" of chlorinated organic substances will be of the order of 3-4 billion SEK for the entire pulp and paper industry. Operating cost increases for the production of sulphate bleached pulp are thought to be in the region of 100-150 SEK ($22-33) per tonne.

The Swedish pulp and paper industry has spent an impressive sum of money in the 1980s on pollution control. Between the period 1980-1987, capital expenditures on abatement have averaged 290 million SEK per annum ($61 million). For the remainder of the decade this will accelerate to 290 million SEK ($64 million).

6.5 Other Canadian Provinces

The pulp industry across Canada is subject to a variety of environmental regulations, mostly based on the traditional pollutants (BOD, suspended solids and acute toxicity). These are similar in concept to the Ontario regulations, but vary with respect to the actual quantities of each pollutant which can be discharged. The levels of compliance and enforcement vary across Canada.

Figure 6.5 shows the progress which has been made by the "average" kraft mill in each province in reducing suspended solids discharges. The Ontario mills have lower discharges than those in any other province except Nova Scotia.

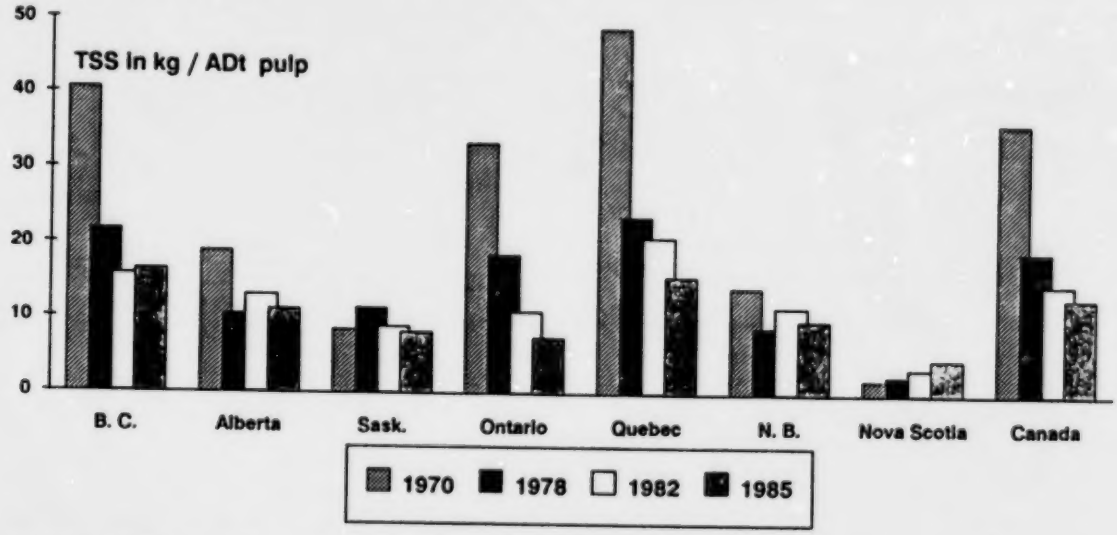

Figure 6.5 Suspended solids discharges for the Canadian pulp and paper industry 1970-1985. (Environment Canada files)

Figure 6.6 shows the changes in BOD discharges for Canadian mills from 1970 to 1980. The "average" Ontario mill discharges more BOD than those of any other pulp producing province except Quebec. As noted in figure 6.2, discharges vary widely from mill to mill.

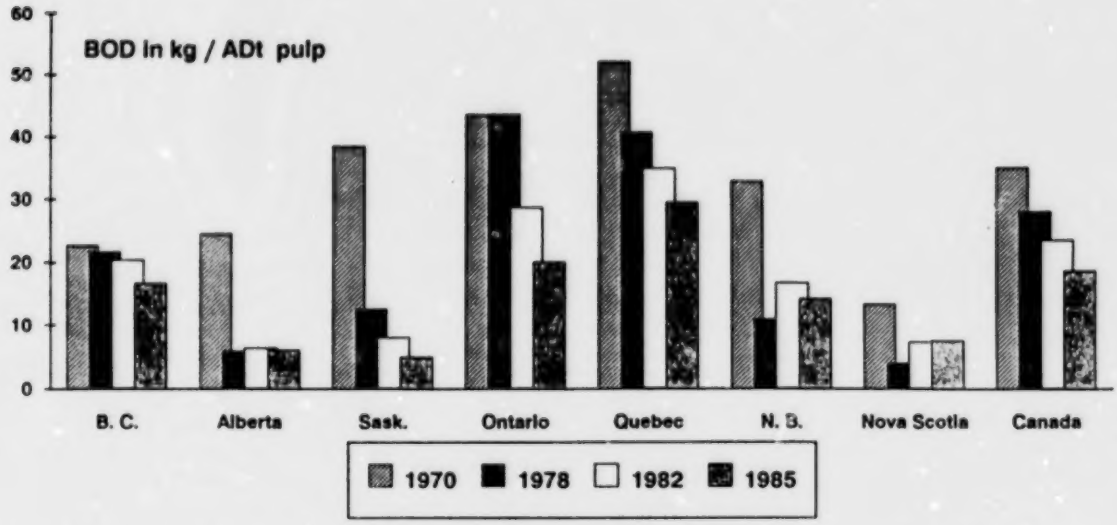

Figure 6.6 BOD discharges for the Canadian pulp and paper industry 1970-1985. (Environment Canada files)

6.6 Comments on Effluent Quality and Regulation in Other Jurisdictions.

SUMMARY. In Ontario the degree to which the quality of effluent from kraft mills has been improved since the early 1970's has been lower than in the US. In Sweden, kraft mills are under very strong pressure to drastically reduce the amount of TOCl emitted into the environment.

Progress in improving the quality of effluent from bleached sulphate pulp mills in Ontario has not been impressive when judged against the progress that has been made in jurisdictions outside of Canada . We have shown that in terms of BOD US mills, under pressure from EPA,and in terms of BOD, US mills,under pressure from EPA and state regulatory agencies, have brought about a much larger reduction in emissions than has been the case in Ontario. There is every indication that the EPA will continue to enforce US regulations and that the regulations will become more stringent. In the control of organochlorines, the US has not made appreciably greater progress than Ontario or Canada.

The Canadian guidelines for fish toxicity were implemented in Ontario many years ago, but only one of nine kraft mills always meets the toxicity requirement. The US lagged far behind in considering effluent toxicity, but in the last four years has moved in advance of Ontario, with much stricter and more comprehensive tests.

In Sweden, and to a lesser extent in Finland, the regulatory approach in recent years has been to switch the emphasis from controlling conventional pollutants to directly controlling the emission of chlorinated organic substances. Presently, mills producing bleached sulphate pulp in Sweden have, on average, lower discharges of organochlorines than in Canada and the US. (The Espanola mill in Ontario and a number of mills in the US have introduced an oxygen stage and biological treatment, and a number are in the process of either converting to oxygen delignification or planning to convert to such a system and so will have organochlorine discharges comparable to the best Scandinavian and US mills.). The Swedish

government has adopted a medium-term target of further reducing TOCl discharges to 1.5 kg per tonne of output by 1992. The Swedish government is reportedly requesting the Finnish government to restrict TOCl emissions from mills in Finland, since a large number of mills in both countries discharge effluent into the Baltic.

7. AQUATIC TOXICITY TESTS

SUMMARY. (1) The lethal test with fish or other organisms is a convenient and relatively fast way of exploring toxicological problems. A stripped-down version of the lethal test is used to monitor effluents. (2) The sensitive newly-hatched stages of fish are now being used as a rapid lethal/sublethal test (mortality and growth) to assess and monitor effluents. (3) The "safe" concentration of a substance or an effluent may be estimated by sublethal experiments which use a whole-organism response of obvious ecological importance, such as growth or reproductive success. Studies of biochemical and physiological effects within the fish allow understanding of the mechanisms of toxic effect, but they are usually less useful for estimating "safe" levels in the environment. (4)The toxicity findings from laboratory tests should be validated by field studies. For pulp mill wastes, that has been accomplished to a large extent by numerous biological surveys in the receiving waterbodies.

The toxicity test for checking pulp mill effluent, using rainbow trout, is a relatively simple type of test. A spectrum of tests is available, and all of them have been used to provide information on toxicity of mill wastes. This section of the report outlines these tests and the purposes they serve. References to the literature have been suppressed; they are available elsewhere if desired, along with more detailed explanation of aquatic toxicology (Sprague 1988).

7.1 General Features of Aquatic Toxicity Tests

It is important to understand that aquatic toxicity tests use constant concentrations of the effluent (or other toxic substance). In that way, it is possible to carry out appropriate analyses of the results. Predictions can then be made to the expected effects of fluctuating concentrations in the real world. It is not feasible to make any general predictions from laboratory tests in which concentrations are allowed to fluctuate.

Accordingly, toxicity tests are carried out with separate groups of fish (or some other organism), each group exposed to one concentration of toxicant as part of a series. If it is a lethal test, the percentage mortalities at the various concentrations can be used to estimate the median lethal concentration or LC50, that being the most precise estimate of effect. The LC50 may be thought of as the concentration of effluent that would just kill the "typical fish". If it is a sublethal test, the degree of effect at each concentration may be assessed, for example the degree of impairment of growth.

Various statistical procedures may be used to show the relationship of concentration and effect, to estimate the lowest concentration that caused a significant effect (the LOEC or lowest observed effect-concentration), or the highest concentration which caused no observed effect (NOEC).

It is also important to recognise that in aquatic toxicology, the duration of exposure is inextricably combined with concentration of toxicant, both being part of the total exposure experienced by the fish.

7.2 Categories of Tests

From a practical point of view, aquatic toxicity tests may be categorised by type and by purpose, as follows.

Lethal tests
- Exploratory tests, for initial or rapid information
- Monitoring or regulatory tests to appraise effluents

Sublethal tests
- Whole-organism effects, for estimating "safe" concentrations
- Within-organism effects to understand mechanisms of toxicity
- Field tests to validate the laboratory findings
- Bioaccumulation as evidence of potential toxic effects

Like all categorisations this one has deficiencies, for example monitoring of effluents is now being done frequently with sublethal tests.

7.2.1 Tests of Acute Lethality

These are relatively short, lasting about 4 days for fish. Mortality is the end-point. Lethal tests are useful for:

(a) establishing an initial benchmark of toxicity for an unstudied effluent or substance;

(b) comparing the relative toxicities of substances or the relative sensitivities of species; or

(c) as a tool for monitoring changes in toxicity of an effluent over time.

Obviously, such tests do not estimate a "safe" concentration, since there would be sublethal effects at lower concentrations. A monitoring test for effluents should be designed as simply as possible for economy, so it is usually a single-concentration test with a simple pass/fail criterion such as allowable percentage mortality.

There are various techniques for carrying out such tests. The simplest is a *static* test, in which batches of toxicant are made up to the desired concentrations, the fish added, and the system is simply allowed to stand for the four-day test. In general the procedure underestimates toxicity because the concentration of toxic chemical weakens as it is sorbed by the fish, the walls of the container, or volatilised. A *renewal* test is a variation in which the test-solution is replaced by fresh solution on a daily basis. In general this is not desirable because the disturbance created by changing causes physiological upset of the fish, which may affect results. Nevertheless, a renewal test is given as an option for a monitoring test in Canadian regulations and guidelines for the pulp and paper industry (EPS 1971, 1972). *Flow-through* tests use a continual inflow of new test-solution to displace the old. They are the most desirable since all conditions of exposure can be kept more or less constant, but they are also more difficult and expensive to carry out.

The rainbow trout (*Salmo gairdneri*) is somewhat of an international standard cool-water fish for toxicity testing. In North America, the fathead minnow (*Pimephales promelas*) is now widely used because it is small, takes readily to the laboratory and breeds in aquaria at any time of year. Thus it is useful for life-

cycle exposures and for providing newly-hatched fish for a sensitive test. Among invertebrates, the same characteristic of easy breeding in the laboratory is leading to frequent use of the freshwater crustaceans ("water-fleas") *Daphnia magna*, *D. pulex*, and *Ceriodaphnia* sp. The last-named water-flea is widely used by the US EPA because an entire life-cycle exposure takes about a week!

7.2.2 Sublethal Tests

These can use almost any response of the test-organism that can be measured, including physiological, morphological, behavioral, etc. They can be divided roughly into whole-organism and within-organism studies. The first category usually yields results which are of obvious significance for the welfare of fish, and recent studies emphasise life-cycle and early life-stage testing. Within-organism tests often involve biochemical research, mostly intended to discover mechanisms of action of a toxicant. Changes found within the organism, say increased levels of an enzyme, cannot necessarily be interpreted as deleterious effects, but may merely be within a normal range of adaptation.

Life-cycle exposures of rats or mice have long been standard procedures in pharmacology, but only in the last two decades have the techniques become common in aquatic toxicology. The usual procedure is to start with recently hatched fish or newly-released water-fleas (*Daphnia*), rear groups of them to maturity at different concentrations of the toxicant, then rear the second generation through a month of early life at the same concentration as the parents. A researcher can estimate the NOEC by assessing many kinds of deleterious effects such as long-term survival, growth, tumors, abnormal behavior, time to maturity, spawning success, as well as mortalities, deformities, and growth among the second generation.

The most sensitive effects in a life-cycle test are almost always seen within the early life-stages, so various "short-cut" methods have been developed, using embryos, larvae, or very early juveniles. Exposures of only one month were sufficient to study those stages in fish, and results were usually very predictive of effects in a full life-cycle test. Even faster techniques give good results. Norberg and Mount (1985) used 7-day exposures of newly hatched fathead minnows, and evaluated only dry weight and mortality, with results similar to those from longer tests. In the USA, EPA is currently using the 7-day test to evaluate effluents and surface waters, because the test is more sensitive than lethality.

Many other sublethal effects have been used. Growth of fish is a straightforward assessment that should integrate all effects within the fish. Maximum swimming performance of fish should be another good integrator of overall damage, but is difficult to measure. Pathology of tissues is widely used in mammals to diagnose toxic effects, but this approach is less successful with fish, mostly because of the surprising variety of abnormalities that are found in "normal" fish. Behavioral reactions can be important because they may be affected by concentrations which do not cause apparent physiological damage. The above effects are meaningful ones for assessing "safe" levels of a pollutant.

Biochemical and physiological measurements within the fish are best used for understanding the mechanism of an effect, not estimating "safe" levels. Although there are numerous papers in the scientific literature documenting "sublethal effects" by "a new and rapid biochemical test", the within-organism changes should not be accepted as evidence of damage unless they have been validated as predictors of meaningful whole-organism effect.

7.2.3 Field Validation

The tests described above are done in the laboratory. Ideally, any estimates of the NOEC or "safe" level of a pollutant should be validated by field studies, to show whether the laboratory estimate is confirmed in a functioning community in a real environment. For example, effects on spawning of individual fish in the laboratory do not necessarily predict what will happen to populations in the wild, and effects on one species in a laboratory are not likely to predict changes in a community containing that species.

Field experiments are difficult to carry out and expensive, and it is difficult to justify polluting a real ecosystem for an experiment. Therefore tests are often done in "artificial ecosystems" which simulate the real world. For example there are some validating studies with pulp mill wastes in "artificial streams".

For pulp mill effluents, important validation has been provided by the hundreds of biological surveys of lakes and rivers receiving mill wastes. Usually these surveys assess the kinds and numbers of invertebrate animals, and often extend this to populations of fish. Less frequently, there are studies of the condition of the fish, maturation, or apparent spawning success judged by numbers of young fish.

7.2.4 Epidemiology

One special field technique that has developed rapidly over the last decade is surveying wild populations of fish for diseases or abnormalities, i.e. an epidemiological approach. External tumours or neoplasms are easily recognised and quantified, and are particularly evident among bottom-dwelling fish. Tumors in the liver are also relatively easy to identify. Such surveys have indicated apparent "hot spots" of tumors in certain polluted inshore areas of Puget Sound and in industrialised rivers.

The frequency of deformities may be assessed, for example twisted spinal columns or eroded fins in fish, or malformation of mouthparts and eyes in aquatic insects.

Abnormal functioning of aquatic organisms is frequently included in surveys using biochemical tests such as levels of activity of selected enzymes. Certain pollutants stimulate production of "defence enzymes" such as the mixed-function oxidases. Biochemical/physiological abnormalities can often be taken as an early warning of stress from pollutants, but as mentioned above, they need correlations with whole-organism effects before they can be designated as harmful findings.

7.2.5 Chemical Approaches

If the toxicology of a chemical is well understood, then that chemical may be monitored by measuring it directly. Concentration in an effluent may be determined and a hazard assessment (see Section 10.4) may be developed for the receiving ecosystem.

If a chemical is persistent and also tends to accumulate in organisms, then its concentration may be measured in fish and other organisms as an indication of danger to those animals or to their consumers. Bioaccumulation is the general term used when an organism takes up a chemical selectively and stores it in the body at elevated concentrations. *Bioaccumulation* may involve uptake from water, food, or both. The *Bioconcentration Factor* (BCF) is the ratio of the concentration of a substance in the fish to the concentration in the water where it has lived. The definition excludes dietary intake, and numerical values of BCF will almost certainly have been derived from laboratory exposures. *Biomagnification* would refer to

accumulation through the food chain, i.e. higher residues at the higher trophic levels because of dietary intake.

The level of residue in an organism depends not only on the rate of uptake, but also on available mechanisms for storage in tissues, and on rates of clearance from the body. Because of concern for human health that could result from eating contaminated fish, there has been a great deal of monitoring, research, and development of techniques.

Tainting is a related problem that can be important with kraft mill effluents. The term has taken on a narrow meaning, and interest is not so much in the concentration of the bioaccumulated substance, but in the off-flavour perceived by a human consumer.

7.3 Monitoring for "Traditional" Toxicity

> *"We need a freeze-dried, talking, fish-on-a-stick."*
>
> John Cairns, Jr., paraphrasing the expressed desires of industrialists, in a keynote speech at a conference on health of Great Lakes ecosystems, 1985.

By "traditional" we mean the acute (short-term) toxicity, such as that measured by the rainbow trout lethal test. To some extent that is related to the more subtle toxicity that concerns us most, such as chronic effects and genotoxicity. Toxicity can only be measured by observing the effect on a living organism. There are existing regulatory procedures for monitoring traditional toxicity and in this section of the report we consider their suitability, and other potentially useful tests.

A monitoring test should be designed to do a very specific job and it should be an efficient vehicle for getting the desired information. It should have most of the following features.

Fast, for rapid feedback in case a toxicity problem needs correction
Sensitive, to detect low-level toxicity
Inexpensive
Single-concentration
Clear-cut criterion to indicate either pass or fail
Small-scale, to avoid large samples and large facilities
Uses an easily-cultured organism of constant sensitivity
Easily run by personnel without extensive training
Results are broadly predictive of toxicity to other aquatic organisms

In other words it should be streamlined, fast, cheap, and give a clear yes/no answer to a defined question of toxicity. It is not a research test, and it should not be adorned with unnecessary extra features, in a misguided effort to dignify it as a powerful research test. Before the test is designed to answer a specific question, it is obvious that the question must first be decided upon! In other words the regulators must decide what level of toxicity is acceptable; then a simple pass/fail test can be designed to see if that level is satisfied.

7.3.1 Ministry of Environment and Canadian Fish Lethality Tests

SUMMARY. (1) The Canadian federal toxicity test for pulp mill effluent is a simple, single-concentration, pass/fail test as is appropriate for monitoring. It requires that not more than 20% of rainbow trout should die in 65% concentration of effluent. (2) The Ontario definition of toxicity appears to be not more than 50% mortality in full-strength effluent, apparently more stringent than the federal one. Ontario's monitoring tests use several concentrations and estimate the LC50. (3) The Ontario test probably underestimates toxicity by a factor of two because it is a static one whereas the federal legal test requires continuous flow of new testwater. (4) The tests should be run at pH 7 or the pH of the receiving water. The effect of pH should not be included in the toxicity test, since it is not a factor in the environment after mixing.

The first toxicity test specified for pulp mills was by the Canadian government (EPS 1971). Those regulations outlined a simple test that had many of the features of a good monitoring test. It was stated that 80% or more of a group of fish must survive in 65% concentration of effluent. If fewer than 80% survived, the effluent was considered "toxic" and discharging it was an offense under Section 33 of the Canada Fisheries Act. The fish was to be a local species, i.e. not necessarily trout. This is a continuous-flow or "flow-through" test, i.e. the testwater is continually being replaced with fresh mixture during the 4-day test. So it is indeed a relatively simple one-concentration, pass/fail test.

The following year, Canadian "guidelines" were issued with more details (EPS 1972). The test mentioned above was defined as a "legal" test, and rainbow trout had to be used, continuous flow was required, and there was to be replication of the 65% concentration, with 5 replicates suggested. A monitoring test was also described. This could be either continuous-flow or "static", although it was "recommended" that the testwater be changed daily in the static test, i.e. a renewal test was suggested, but was apparently optional.

The elaborations in the second document created some inconsistencies. The legal test with continual replacement of the testwater would show an effluent to be about twice as toxic as a monitoring test carried out as a static test (i.e. no replacement of water, Walden et al. 1975, see Section 7.5.1).

Turning to Ontario, the recent control orders for kraft mills issued by MOE usually state, for toxicity, that the effluent must satisfy the toxicity requirements under the Canada Fisheries Act, i.e. those outlined above. Sometimes it is required that full-strength effluent should not be lethal to more than 50% of a sample of fish. The Ministry does not carry out tests with the federal single-concentration procedure, but with a multi-concentration test so that the LC50 can be estimated. Certainly this provides more information, namely the degree of toxicity of each effluent, but the more complex procedure adds to the expense of monitoring. Such a multi-concentration static lethal test with rainbow trout currently lists at $340 when done by consulting companies.

Ontario defines toxicity differently from the federal regulation. Any effluent "tested according to the following protocol that produces a 96-hour LC50 of less than 100% concentration shall be considered acutely lethal to fish" (Craig et al., 1983). The protocol mentioned is a 4-day static test with rainbow trout. In other words, the requirement is that full-strength effluent should not kill more than 50% of the fish. This is thought to be "at least as stringent as the federal baseline requirements" (MOE, 1987b).

Ontario has, however, apparently built in a two-fold weakening of requirements by using static tests, i.e. no renewal of test-solutions (further discussed in Section 7.5.1). The static procedure is described in the

Ministry of Environment protocol (Craig et al., 1983), and we have visited the excellent laboratories at MOE Rexdale and Thunder Bay (Lakehead University) to verify that static tests are in use for monitoring effluents.

7.3.2 Comments

(1) There is a modest degree of confusion in the monitoring procedures with rainbow trout, and in the regulatory implications of the tests. We have adopted an interpretation, taken from the wording of several Ontario control orders, that mills should satisfy the federal "legal" test, i.e. the continuous-flow test. That seems reasonable since Ontario has no formal legislation of its own, requiring non-lethal effluents.

(2) The federal documents did not explain the rationale for selecting the 65% concentration and 80% survival. We understand that the authors of the test were working from information that a biotreated effluent be non-lethal at 65% concentration, 8 times out of 10. In other words the specifications were based on available technology. The implication behind regulatory standards based on a lethal test is that if an effluent is not acutely lethal, then after reasonable dilution it will probably not cause sublethal effects.

(3) Much of the apparent toxicity of kraft mill effluent can be caused by pH. The pH would not be a problem after discharge, since a small amount of dilution would bring pH close to that of the receiving water. We consider that this is not the type of toxicity that should be looked for or monitored, and therefore **recommend** that regulatory tests with kraft mill effluent be carried out in test-mixtures that are either pH 7, or the pH of the water that receives the waste. The federal guidelines say nothing about adjusting the pH, nor does the MOE rainbow trout protocol (Craig et al., 1983), and the routine tests of the MOE use unadjusted pH.

7.3.3 Other Tests for Monitoring Acute Lethality

The second most widely used group of organisms in North American aquatic testing includes the water-fleas *Daphnia* or *Ceriodaphnia* sp. which are useful because of their small size and rapid life cycle. The Ministry's toxicity lab at Rexdale routinely uses *Daphnia*, but we do not recommend this genus for tests with kraft mill effluent, since they are generally less sensitive to it than are trout (see Section 8.1). For other toxicants or other kinds of effluent, *Daphnia* may be more sensitive than fish. For example *Daphnia magna* was twice as sensitive as fathead minnows to the lethal effects of sewage effluent (Kimerle et al. 1986).

On the other hand, the very small water-fleas of genus *Ceriodaphnia* would seem to be useful for testing pulp mill wastes. From all indications, they are quite sensitive to lethal effects of many chemicals and also effluents. For example *Ceriodaphnia* was 4 times as sensitive as the fathead minnow to municipal sewage effluent (EPA 1985X), and much more sensitive than the fathead to polluted waters from 10 locations in the Cuyahoga River, Ohio (EPA 1987Z). There is the further advantage of this genus that it can be used in very rapid (7 days) sublethal tests with mill effluents as described in Section 7.4

There have been difficulties in rearing *Ceriodaphnia* leading to some very strong complaints from people in the paper industry (Kraus and Kornder 1987). However efforts to identify and remedy the problems have been organised (DeGraeve and Cooney 1987) and apparently solved, according to various personal contacts we have made.

7.3.4 Rapid Tests with Micro-organisms

SUMMARY. (1) There are rapid new toxicity tests based on reactions of bacteria, which can be run almost as if they were chemical tests with bottled reagents. They are reasonably consistent with results of other methods of testing toxicity, and seem to be somewhat more sensitive to pulp mill effluent than the lethality test with trout. (2) If these tests are used in mills, there should be great benefits in finding toxic streams and reducing toxicity in general, because of the ease of doing the tests and the rapid feedback on results. (3) We recommend that the Ministry encourage the use of a suitable rapid test or tests by awarding recognition as one accepted way of measuring toxicity.

In recent years certain very rapid tests (hours or minutes) have been developed and offered as "kits" on the market. We are much taken with these tests because their rapid feedback of information makes it possible for mills to make major improvements in toxicity of their effluents. Mill personnel could make frequent checks of toxicity, daily if desired, and detect any developing problems at an early stage. Specific sources of toxicity within the mill could be tracked down at little expense, with the objective of reducing or eliminating those sources.

The two examples of such tests described below, are carried out in a manner that is similar to a chemical test, with pipetting and readings of colour or light produced. The freeze-dried bacteria may be kept in a freezer and reconstituted when desired. The procedures are very standardised.

Thus the tests meet many of the criteria for a monitoring test, listed at the beginning of this section. The real advantages are speed, elimination of the need to culture organisms, small scale, and standard technique that can be used by ordinary technical personnel. Low cost can be a feature. The main drawbacks, discussed below, could be that the tests are no more sensitive than trout lethality, and the question about whether the results are predictive to the effects on other organisms. A number of microbial tests are available (Dutka and Kwan 1981) but two standardised commercially-available ones are described below.

One test available as a kit is the "Toxi-Chromotest" which detects damage to the enzyme-manufacturing ability of the bacterium *Escherichia coli* (Bio-Response Systems Ltd., P.O. Box 2564, Station M, Halifax, N.S. B3J 3N5). A simple colour test is used to show which concentrations of toxicant reduce or eliminate enzymatic production. A kit currently costs $280, and a typical test could be run for less than $20. Certain laboratory equipment such as an incubator is also required. The test looks useful and meaningful, but we have not yet seen this test in operation, nor have we seen any evaluations in the scientific literature or heard from a Canadian user.

A more widely known rapid test is "Microtox", which measures the reduction in production of light by the luminescent marine bacterium *Photobacterium phosphoreum* (Microbics Enterprises, P.O. Box 1235, Forest, Ontario, NON 1J06V0). The usual exposure is for 15 minutes. The standard procedure is to estimate the IC50 (Concentration for Inhibition of 50% of the luminescence) or the IC20, so it is not a single-concentration test. The equipment costs about $25,000, but the running cost per test would be in the vicinity of $20.

There is now an extensive literature on Microtox, and in general we conclude that the test is about as sensitive to a variety of toxicants as a lethality test with fish (De Zwart and Sloof 1983, Bulich 1986). The bacterium used in the test is not a fish, of course, so the two types of organisms do not necessarily

correlate well in their responses to different toxicants, but the differences do not appear to be any worse than those which show up among tests with fish, *Daphnia*, and algae, for example. Unpublished results from the EPA laboratory in Corvallis, Oregon indicate that Microtox and Toxi-Chromotest differ widely in sensitivity to various chemicals, but are roughly similar in average sensitivity.

There is some direct information on Microtox tests with pulp mill effluents, and it appears to be somewhat more sensitive than lethality tests with trout.

The most thorough tests involved some fifty effluents from a variety of pulp and paper mills (Blaise et al. 1987). Microtox agreed with the trout lethality test 84% of the time, and with an algal test 90% of the time. The algal test was most sensitive, Microtox was next, and the fish test was appreciably less sensitive. Blaise and colleagues compared two (unspecified) pulp mill effluents, and found that Microtox was 4.4 times and 7 times more sensitive than a rainbow trout lethality test, and 14 times more sensitive than lethality with the water-flea *Daphnia magna*. Unpublished Swedish work showed that Microtox was 2 - 3 times as sensitive as *Daphnia*, tested with various kinds of bleach plant waste, and averaged 5.3 times as sensitive as trout LC50s for bleached and unbleached kraft mill effluent (personal communications, P.A Solyom, Swedish Environmental Research Institute, Stockholm, and B.-E. Bengtsson, Swedish Environment Protection Board, Studsvik).

One of the main criticisms sometimes aimed at the Microtox test is its relevance. "It is a marine organism." We agree, but do not see any disadvantage since marine organisms tested in sea-water are usually of much the same sensitivity to toxicants as are freshwater organisms tested in fresh water (Sprague 1985). "This bacterium does not predict effects on fish." We agree to some extent but point out some correlation as discussed above. Of much greater importance is the concept that the aim of these pollution control exercises should be to protect aquatic ecosystems, not one group such as fish. For that reason there is great emphasis today on a battery of tests using, say, a fish, an invertebrate, an alga, and a micro-organism. Often the micro-organism is the most sensitive, and a very strong case has been made for always including a bacterium (Sloof et al. 1983). "Does the reduced production of light indicate a harmful effect? Is it meaningful, even for the bacterium itself?" That question is a good one and does not seem to have been answered. The effect can be regarded as one that has been empirically related to toxicants and their concentration. At the technical level, standard Micrctox procedure goes only up to effluent concentrations of 50%, and a special adaptation is used for coloured effluents such as kraft mill effluent.

We see huge advantages in having mills able to test toxicity on-site, with nearly immediate results. Some Canadian mills already have Microtox, and at least four units are used by the paper industry in Ontario. This can only lead to more interest in toxicity problems and improvements in them.

We are therefore recommending that the Ministry encourage the use of a rapid test or tests of this kind in the pulp and paper industry. Results of the tests should be given official recognition as monitoring results. MOE might wish to compare relative toxicities of mill effluents as indicated by the rapid method or methods and by trout LC50s. We pessimistically expect that this recommendation will be dismissed by old-line regulatory people because the test is not based on a fish. Such ingrained prejudice may take some time to die out. We can only repeat that the ultimate objective of aquatic toxicity testing is to protect ecosystems, and fish are not always, or even usually, the most sensitive organisms in an ecosystem.

7.4 A Policy of No Sublethal Effects Beyond a Mixing Zone

SUMMARY. (1) The Ministry should phase in a policy that requires no overt sublethal effects of kraft mill effluent, beyond the edge of a mixing zone. (2) Compliance should be checked periodically (yearly?) by laboratory tests on growth of newly-hatched fathead minnows or reproduction of the water-flea Ceriodaphnia, or both. (3) A similar program, perhaps even more infrequent, should measure the genotoxicity of effluents. (4) The programs should be tied in with field surveys of dilution of effluents, and biological effects on the surrounding aquatic communities. (5) The Ministry is already doing all of these things to some extent, under various projects or programs. (6) The program should be actively led at a high level of management, to integrate the various groups of people involved, to ensure that decisions were reached on whether sublethal effects were absent, and to ensure that action was taken if necessary. (7) Such a policy requires definition of mixing zones, and that should be done on the basis of surface area affected.

Monitoring with acute tests usually gives a rough reflection of the sublethal and chronic effects that are of ultimate concern. The Ministry should continue its program of testing acute lethality of effluents. However there should be, in addition, a deliberate move to eliminating sublethal and genotoxic effects beyond a restricted mixing zone for kraft effluents.

Definite sublethal tests should be selected and specified for use in the control program. The wide choice of sublethal tests, is described in Section 7.2.2, the sublethal research on kraft mill effluent is summarized in 8.2, and mutagenicity is reviewed in Section 8.5. Clearly the choice will go to the newer "short-cut" sublethal tests, and a variety of them have been proposed. A Canadian test requires only 4 days for an exposure that covers the complete life-cycle of a nematode worm (Samoiloff et al. 1980). A 14-day exposure of adult zebra fish to kraft bleaching effluents is 5 times more sensitive than exposures involving only young stages of fish, because of effects on developing gametes (Landner et al. 1985).

In selecting tests, there are advantages in choosing ones that are already in use on pulp mills on the other side of our lakes and rivers, in USA. (Section 6.4.2). We therefore suggest that a laboratory test based on young stages of the fathead minnow (Pimephales promelas) be periodically used by MOE to test the waste from each mill. We recommend the 7-day "Larval survival and growth test" of Norberg and Mount (1985; also Horning and Weber 1985). The Ministry already has expertise in these tests in its Rexdale Aquatic Toxicity Unit (Dr. C. Neville), and many mill effluents have apparently already been tested, although we have seen no reports of the results.

We recommend that a second test be used at the same time of checking an effluent, namely the 7-day life-cycle and reproduction test with Ceriodaphnia sp. (Horning and Weber 1985). It may be that one or other of these sublethal tests would prove superfluous.

A similar program should be carried out to assess genotoxicity of the mill effluents. The Rexdale laboratory also has excellent capability in this field, and D. Rokosh should be asked to design a program and support should be provided. This testing need not be frequent either, and in fact might be limited to one thorough examination of each effluent, repeated if there are changes in process at the mill.

The purpose of the sublethal testing in the laboratory would be to detect any danger of subtle effects on ecosystems receiving mill effluents. Having determined the lowest effect-concentration and the no-effect concentration in the laboratory (LOEC and NOEC), that information must be compared with good survey

data on dilutions of the effluent at the edge of a defined mixing zone. The resulting estimate of the degree of effect and area affected should be compared with results of biological survey at the discharge site.

The field work at the site should follow conventional approaches, and Ministry personnel are well-versed in these. There should be physico-chemical studies of dispersion, and biological surveys of benthic invertebrates and fish populations. Such surveys are expensive but they need not be frequent. If results were favorable there would be no need to repeat unless mill processes or production changed. It would be highly desirable to supplement those approaches with caged fish studies (mortality, bioaccumulation, see Inniss et al. 1978), and surveys of fish with tumours or malformations (Malins et al. 1988).

Much of the work described above is already being done under various programs and projects of the Ministry and co-operating agencies. We are suggesting (a) that it be formalized by incorporating the "no-sublethal-effects" requirement into regulations and control orders, and (b) that there be assurance of integration of the various parts.

To successfully control sublethal effects form kraft effluents, such a laboratory and field program clearly requires vigorous direction and integration from a fairly high managerial level. It would require considerable sharing of results and co-operative efforts by different laboratory, field, regional, and managerial groups in MOE. It is no good to just carry out the laboratory toxicity tests, and file them away or put them into a report, if the information is not used. Having made an integrated assessment of environmental impact at a site, it must be followed by an appraisal and decision at managerial level, about the acceptability of any damage, and suitable action should be taken on any negative decisions.

We feel that such a broad-spectrum sublethal program would complement the present program of acute testing, and would focus on the more important subtle effects in the waters receiving kraft mill wastes.

7.4.1 Defining Mixing Zones as Limits of Sublethal Effects

Obviously, if there is to be a policy of no overt sublethal effect beyond the edge of a mixing zone, then that zone must be defined. It is a difficult topic and there is no universally accepted solution. Historically, the Ministry has defined mixing zones on a case by case basis as required (MOE 1984). In practice that has often meant that in rivers, the water quality objective should not be exceeded at any point that is more than half way across the width of the river. The definition of a zone in lakes is less obvious.

In the USA., many states have a similar requirement for rivers, that the mixing zone should not occupy more than one-quarter or one-third of the cross section of the river (EPA 1985X). Few of the states specify the downstream length of the mixing zone. Mixing zones in lakes are specified by only a few of the states, mostly as 10% of the surface area of the lake, or a fixed distance for radius of the zone.

We agree with, and recommend, the suggestions for definition of mixing zones that are given in the "Hanna report" to MISA (Hanna et al. 1987). In essence, that means defining the size of the mixing zone on the basis of surface area of the body of water. Maximum longitudinal and lateral extent of the zone should be specified, and also a maximum length of impacted shoreline and provision to prevent overlap with sensitive areas or uses.

Many of Ontario's kraft mills discharge into lakes, and mixing zones would have to be of appreciable size. For example, a discharge to Lake Superior with an excellent diffuser had a 50:1 dilution outside an area of 0.006 km^2, which represents a rectangle 80 m on a side (Craig et al. 1986). That would not represent a

suitable mixing zone since the 2% concentration of effluent might have sublethal effects. Dilution to 1% required a much bigger area, equivalent to a rectangle 120 m by 1000 m. A proper diffuser with appropriate location is of primary importance to minimize the area of sublethal effects.

7.5 Encouraging Inplant Control by a Fixed Water Allowance for the Toxicity Test

SUMMARY. (1) Water use by bleached kraft mills has been reduced by more than half over the last two decades. That is highly desirable since it goes hand in hand with good process control and reduced loss of chemicals as pollutants. (2) The toxicity test should encourage water conservation and discourage mills from "diluting" the toxicity test, such as by continuing old practices of heavy water use. (3) We therefore recommend a fixed water use of 250 m^3 per tonne of air-dried pulp produced, to be incorporated into the regulatory test based on trout lethality.

As a committee we are strongly aware of the benefits of close control of processes in the mill to prevent losses , of toxic chemicals, and other substances to the effluent. The concept was important in many of our decisions and recommendations.

A distinctive thing about kraft mills is that they must recycle or burn at least 90% of their potential pollutants, simply to remain economically viable. Clearly, if even more of the material in the mill can be prevented from escaping, there is a saving in the cost of replacing it and a saving in not having to give it waste treatment. Similarly, if dangerous organochlorines are produced in the mill and we rely on waste treatment to take them out, there can be the problem of persistent toxicants in the sludge, and the question about where to dispose of the sludge. These are some of the reasons why, in other parts of the report, we have not emphasised or recommended secondary waste treatment. If equivalent results can be attained by inplant mill control, that is beneficial for all parties including the environment.

One sign of good control of mill processes is reduced use of water. Good operation and control of chemicals is almost always accompanied with lower water consumption by the mill, although those things are not necessarily in direct proportion. We are encouraged that there has been considerable progress in this regard in the past two decades. For example the five mills whose predominant product was bleached kraft mills that were operating in Ontario in 1970 had an average water use of 257 m^3/tonne of air-dried product, but in 1986 the same five mills averaged 120 m^3/tonne, almost exactly half (Table 7.1). From personal experience one of the committee knows that the 1970 values were grossly underestimated, because of poor measuring equipment, but we will use the published figures.

Some components of the waste such as bleach plant effluent are not recycled, and other chemical control may not keep pace with reduction in water use. Thus the toxicants can become more concentrated in the effluent, and therefore the effluent toxicity appears to increase as measured by standard fish tests. This is a rather foolish situation, because the **amounts** of toxic substances discharged to the environment could be substantially lower.

Since the MISA program is particularly concerned about persistent toxicants, we might consider them as an example in considering the rationale involved. Is it better to discharge a low-volume effluent with strong concentration of a persistent, bioaccumulative organochlorine, or a large-volume, watery effluent with a weak concentration of the organochlorine? There is no proper answer to that question because it gives no indication of the amount of organochlorine being discharged. That is precisely our point; **it is the total amount of the dangerous substance put into the ecosystem that is important in the long run, not its concentration in the effluent, which is measured by the fish toxicity test.**

Table 7.1 Effluent Flows, m^3 per tonne of air-dried pulp. (Data from CPPA Mill effluent re-survey, Dec. 31 1970, and MOE 1987)

	1970	1986
Dryden	393	76
Terrace Bay	231	104
Espanola	235	90
Marathon	228	148
Smooth Rock Falls	199	183
Average	257	120

The principle is not very startling since it is already used in the federal regulations to control BOD and suspended solids input from pulp mills. Those substances are regulated in terms of amount allowed per tonne of pulp produced. It makes sense to regulate persistent toxic substances in the same way. The approach is essentially that of "Toxic Units" and "Toxic Emission Factors" (see Section 8.8), i.e. a measure of the amount of toxicity produced per tonne of pulp.

We are dismayed that the Ontario and Canadian governments have failed to adopt this system, and have thus fallen so far behind the approaches used by other groups. Even the US uses the system and in the "Technical Support Document ..." of EPA (1985X), Toxic Units are defined on page 1, and their merits are described. The toxic unit concept was used to sort out waste loads at a Swedish pulp mill 50 years ago (Bërgström and Vallin 1937), and is still used in the Scandinavian industry (Priha and Talka 1986). Some Canadian government biologists have used and recommended the system for pulp mills (Wilson et al. 1976?), and many years ago one of us wrote a report for Environment Canada recommending that pulp mills should be regulated by amount of toxicity, not concentration (Sprague 1974). Still there has been no official adoption by governments in Canada.

Industry shows no such hesitation and in papers published by pulp and paper workers, it is common practice to write about Toxic Units, Toxicity Emissions, and amounts of toxicity. For example it is the standard technique adopted for inplant studies of toxicity in Ontario kraft mills (e.g. Naish 1975, Scroggins 1986), and we repeat some comments from such studies.

"..... the effects on final effluent toxicity .... can only be quantified through the application of the Toxic Contribution concept. This is the only rational means of allocating the net effluent toxicity ...."

"There is no mention of specific water use in the federal regulations. The [toxicity] test is .... based on concentration, which .... is a disincentive for mills to close their water circuits. This is illogical." (Sikes et al. 1983)

An almost despairing complaint came in another study of mill toxicity. "The foregoing shows that the mill has made significant strides in reducing the discharge of toxic substances since the change of ownership in 1983 [35-45% less than the previous amount of toxicity]. Nevertheless, the effluent today is no closer to meeting the federal government's standard for a non-lethal effluent because of the nature of the test procedure which is concentration dependent" (Craig et al. 1986).

The current regulation based on a fish toxicity test, then, actively discourages mills from reducing water use. That is exactly the opposite of what should be happening.

If a mill has a toxicity problem, the current toxicity test would encourage the mill to retain any old-fashioned, high water use practices, inasmuch as that would tend to dilute the toxicants and cause an apparent lowering of toxicity as measured by concentration.

Any such "solution by dilution" should be actively discouraged, and we are therefore strongly recommending that the fish toxicity test should be tied to a fixed maximum use of water per tonne of pulp. Since the federal fish toxicity test has not changed since it was set up for pulp mills in 1971, the intent of the regulators who set it up would be accomplished by setting the maximum allowable water use for a bleached kraft mill at that which prevailed at the time, i.e. 257 m^3/tonne, or say 250 as a round number.

This recommendation keeps the toxicity requirement as strong as it was in the federal regulations of 1971. At the same time it has the highly desirable effect of encouraging mills to look to the processes within their mill for control of toxicity, and to reduce water use and loss of chemicals. Accordingly the emphasis will shift to reducing total amounts of toxic chemicals discharged, in keeping with MISA objectives. Carrying out the federal toxicity test with its single concentration (65%) would require an adjustment of the effluent volume, to the fixed allowance . For the current MOE practice of estimating LC50s, the adjustment could be done by calculations on paper afterwards.

7.5.1 Compensating for a Lenient Testing System in Ontario

SUMMARY. (1) The Ministry customarily uses static toxicity tests to monitor kraft mill effluents, and they probably show only about half of the toxicity that would appear in the flow-through test which is specified in the Canadian regulations. (2) Ontario is stricter, however, in using a higher concentration to define toxicity (full strength effluent). (3) Combining those two factors indicates that the Ontario test is less strict than the federal one by a factor of 1.5. If the Ministry continues with its present static test methods as seems convenient, the fixed water allowance for purposes of assessing toxicity should be 175 m^3/tonne of pulp.

We have recommended above that the toxicity standards for kraft effluent should not be relaxed from the way they were set up in 1971 by the Canadian regulations (EPS 1971, see Section 7.3.1). Ontario specifies

in some control orders to mills that toxicity must meet those federal regulations. Some control orders, however, have an apparently stricter requirement that full-strength effluent should not kill more than 50% of a sample of fish. In other words, the LC50 must be equal to or greater than 100% effluent, which is in fact, the Ministry's usual definition of acute lethality to fish (Craig et al. 1983).

The differences in detail between the federal regulatory ("legal") test, and the usual test procedures used by the Ministry, are confusing and it is not at all clear what degree of non-lethality is being enforced. We urge the Ministry to make the Ontario and federal standards for non-lethality of effluents mean the same thing. We attempt, below, to compare the two and to produce a correction factor which can be used to unify they toxicity standard.

For purposes of comparison, the federal test should be brought to an LC50, from its present requirement that not more than 20% of the fish should die in 65% concentration of effluent. That can be done by using the standardized relationship for mortality and concentration provided by specific research on bleached kraft mill effluent by Walden et al (1975). No other authors have covered the topic so directly and usefully. From that research, the above percentages are equivalent to a federal requirement that the LC50 should not be less than 73% effluent in a flow-through test.

> (The details of the calculation are these. Walden et al. (1975) did lethal tests, then translated results from effluent concentration to Toxic Units (100% / LC50 in % = Toxic Units). By definition, the LC50 then occurs at 1.0 Toxic Units. Different effluents fell along the same probit response line, and 20% mortality occurred at 0.89 Toxic Units.
> Therefore, full-strength effluent that just met the federal regulation, would have 0.89 / 0.65 = 1.37 Toxic Units.
> By substituting in the above formula that defines Toxic Units, the LC50 of full-strength effluent may now be calculated:
> LC50 = 100% / 1.37 = 73% effluent.
>
> This LC50 of 73% effluent may be used as the federal requirement, and compared with the Ontario test which is based on estimation of LC50s.)

The lenient part of the Ontario toxicity test is the use of static tests, i.e. the test-solutions are made up at the beginning of the test, and not renewed for the 4-day duration of the exposure. Various toxic components of the effluent may decompose, volatilize, or be sorbed by the fish or the walls of the tank. The end result is that concentrations of toxic materials are decreasing in the test-tanks during the four days, making the effluent appear less toxic than it really is. For very toxic pulp mill effluents, a static test may show only a quarter of the toxicity demonstrated by a flow-through test, although there may be little difference for mildly lethal effluents (Loch and MacLeod 1974).

The most detailed and useful comparison is, again, that of Walden et al. (1975). They showed that typically, a static test was lethal at 2.0 of the flow-through Toxic Units, i.e. it revealed only half of the lethality. Thus the Ontario test requiring an LC50 of at least 100% in a static test, is equivalent to an LC50 of 50% in a flow-through test.

Based on this research, the Ontario procedure would be less restrictive than the federal one by the ratio of the two LC50s, i.e. 50% / 73% = a factor of 0.68. Alternatively, one could take the reciprocal, and conclude that the Ontario test is 1.47 or one-and-a-half times more lenient than the federal regulatory test.

Since our objective in the preceding section was to arrive at a fixed allowance for water use, that would maintain a strict enforcement of the 1971 Canadian toxicity guidelines, we must obviously allow for the apparent difference caused by the Ontario test-procedure. The Ministry procedure with rainbow trout seems firmly established with a static exposure, and we agree that the procedure is a convenient and economic one. There seems no reason why the Ministry should not continue monitoring with static tests. We will therefore adjust the fixed water allowance to allow for the Ministry procedure.

The water use in 1970 averaged 257 m^3/tonne of bleached kraft pulp (Section 7.5). Applying the best-estimate factor of 0.68, we recommend a fixed allowance for water use of 257 x 0.68 = 175 m^3/tonne, with toxicity tested by the Ministry's standard static rainbow trout procedure.

In making this recommendation, we are aware that other data could be used to make other, somewhat different calculations. For example, a tabulation of results from 496 lethal tests with effluents yielded a certain median value for the slope of the relationship between concentration and % mortality (LC50 / LC1 = 0.615, EPA 1985X). That would indicate that the Canadian federal regulatory test was equivalent to an LC50 of 78%, somewhat different from the 73% estimated above. As another example of an alternate approach, a comparison of 24 pairs of tests showed that static tests were, on the average, only 0.71 as toxic as flow-through tests (EPA 1978). However the comparisons were for individual chemicals, not effluents, so the comparison that we used above, specifically based on bleached kraft mill effluents, would seem more likely to be correct.

We realize that our correlation between the federal and Ontario tests hangs on a single published paper (Walden et al. 1975). There may be disagreement with the exact conversion. If desired, further research could be done on the particular static/flow-through relationship for kraft mill effluents. There is no need for controversy, however. Any mill that feels our recommended water allowance of 175 m^3/tonne is not equitable must be allowed the option of testing with the higher water allowance using the flow-through test with 90% molecular replacement of test-water per 10 hours, as specified in the federal regulations.

7.5.2 The Water Allowance and Toxicity Rating of Ontario Kraft Mills.

A more rational appraisal of the relative control of amounts of toxicity discharged per unit of production is obtained by applying the fixed water allowance to recent data from Ontario mills. The calculations in Table 7.2 take values for water use from Table 6.2, and for actual LC50 from Table 8.1.

For mills with a high water use, or moderate water use, the fixed allowance makes relatively little difference to the estimate of toxicity (e.g. mills D, E, and F). For some mills with moderate water use, the allowance could show that they were generally meeting the intent of the regulations, to control the amounts of toxic substances discharged, to reasonable levels. Mill B, for example, would probably meet the non-lethality standard most of the time, and that would no doubt encourage further conservation of water and process control to achieve the additional reductions of amounts of toxicants, to meet the lethality standard.

Table 7.2 Calculation of LC50s adjusted to a standard water use, for 1985 and 1986 measurements at kraft mills in Ontario.; "Greater than" symbols indicate that the mean includes LC50s of 100% or greater (i.e. non-lethal).

Mill	Water use m^3/tonne of pulp	Water allowance factor	Actual geometric mean LC50 1985	1986	Adjusted LC50s 1985	1986
Six mills without secondary treatment						
A	104	1.68	41%	29%	69%	49%
B	126	1.39	>68%	>67%	>94%	>93%
C	103	1.70	26%	28%	44%	48%
D	148	1.18	12%	13%	14%	15%
E	183	0.956	26%	35%	(25%)	(34%)
F	135	1.30	>66%	>36%	>86%	>47%
Three mills with secondary treatment						
G	61	2.87	13%	21%	37%	60%
H	76	2.30	28%	20%	64%	46%
I	90	1.94	>100%	>100%	>194%	>194%

It is for mills with low water use that the fixed allowance makes the greatest impact in rationalizing our judgement of the effluent, and mill G is a strong example. The actual LC50s of 13 and 21% would persuade an observer that mill G ranked among the worst kraft mills in the province for toxicity, despite the fact that secondary treatment had been installed. Such an apparently dismal performance would of course be disheartening to the operators. Allowing for the commendably low water use, however, raises the adjusted LC50s to the vicinity of 40 - 60% for 1985 and 1986, which is a middle ranking for toxicity among the mills. That gives some better appraisal of how much toxic material is being discharged, and also some hope that further efforts could result in even further improvement that would meet the recommended toxicity assessment, and would meet the intent of the 1971 federal regulations.

For mill I, with low water use and an already non-lethal effluent, the fixed allowance has little effect except to indicate to others what can be achieved.

Much of the action required to control accidental losses can be described as good housekeeping or "running a tight ship", since many dumps and spills are due to simple errors which are relatively easily avoided. The most advanced technology and exotic equipment is ineffective if it is poorly operated or maintained.

Operating practices and training have an important impact on all aspects of mill operations, but particular attention is required to the control of accidental losses. Historically, much of the operator training in the pulp and paper industry has been based on the operating manuals provided by the suppliers of the equipment. While this can be effective in attaining production levels and meeting product quality specifications, it is less satisfactory with respect to the control of accidental losses, whether

environmentally significant or not. Control of these losses requires an appreciation of the overall process system, as well as an understanding of what materials should, or should not, be discharged to the sewer, and the procedures to follow in the event of unforeseen difficulties.

Personnel training for control of accidental losses requires a specific training manual (or section within more general training manuals) and program, prepared by professionals who have the necessary knowledge of process operation and environmental protection. Separate training is required for shift operators, operating supervisors and maintenance personnel. Some pulp and paper producers have developed this expertise in-house, while others prefer to retain external consulting firms to prepare such manuals and training programs.

8. TOXICITY OF KRAFT MILL EFFLUENTS TO AQUATIC ORGANISMS

8.1 Acute Lethal Action of Whole Effluents

SUMMARY. (1) Most kraft mill effluents with only primary treatment are lethal to fish. However these wastes are only mildly toxic and would not normally cause direct mortality, given adequate dilution in the environment. (At least 2 Ontario mills have unsatisfactory toxicity conditions because of poor mixing or insufficient dilution water.) (2) For the 6 Ontario kraft mills with only primary treatment, lethal concentrations typically ranged from 12% effluent to non-lethal. (3) Secondary (biological) waste treatment may or may not render an effluent non-lethal. Of the three Ontario kraft mills with aerated lagoons, one had a consistently non-lethal effluent, but the other two mills had effluents that were as lethal as untreated effluents. (4) Fish are among the most sensitive aquatic organisms, judging by resistance to lethal levels.

Most kraft mill effluents will kill fish, whether the effluent comes from a bleached or an unbleached plant, and whether or not it has received primary waste treatment. The lethal concentrations are, however, quite variable. McLeay (1987) lists tests against rainbow trout, and LC50s ranged from 3% to 100%. A geometric mean would be in the vicinity of 16% whole effluent. The variation between mills cannot really be correlated with particular processes in the mills, although mills operating on softwood usually have a more toxic effluent. More than likely the control of spills and general tightness of operation account for much of the variation.

Secondary waste treatment reduces lethality but does not necessarily eliminate it. McLeay lists 9 such mills, of which 6 were sometimes lethal to rainbow trout.

Ontario kraft mills are not greatly different from that general pattern, as shown by the Table 8.1. Of 6 mills without secondary treatment, the geometric mean LC50s from tests in 1985 and 1986 were >34% and >31%. The values are "greater than" because two of the mills were non-lethal in some tests, i.e. values of >100% were used in calculating the means. (One of those mills was lethal in 11 of the 17 tests in two years, and the other was so in 3 out of 5 tests.) Three Ontario kraft mills have secondary treatment, and one has been non-lethal for years. The other two are normally lethal with geometric mean LC50s of 19% and 21% effluent in the two years (MOE 1987a,b).

Some other things may be noted in the Table 8.1. The mean values, at least, were reasonably consistent from year to year at each mill. Two of the mills with secondary treatment produce (at least up to 1986) an effluent that was quite toxic; the geometric means were lower than those for mills without secondary treatment (i.e. lower LC50 = greater toxicity). Clearly the installation of aerated lagoons is not necessarily an instant cure for lethality. The non-toxicity of the third "treatment mill" required some care to achieve, as discussed in Section 5.3.

The acute toxicity of kraft mill effluent is actually rather mild. We may compare with other pollutants that are customarily measured, not in percentage concentration, but in mg/L or "parts per million". For example, zinc salts are a moderately toxic being lethal to fish at about 1 mg Zn/L. On that scale of measurement, our mean value for untreated kraft mill effluent (30%) becomes 300,000 p.p.m., or 5 orders of magnitude less toxic than the zinc.

Table 8.1 Geometric mean (gm) LC50s of whole effluents from Ontario kraft mills. There were 1 to 10 toxicity tests per mill per year.

6 mills without secondary treatment		3 mills with secondary treatment	
1985	1986	1985	1986
41%	29%	13%	21%
>68%	>67%	28%	20%
26%	28%		
12%	13%	gm 19%	21%
26%	35%		
>66% (1984)	>36%	>100%	>100%
gm >34%	>31%		

Acute lethality to fish would not be expected in the receiving water, given a location with reasonable opportunity for dilution and a mill operating under normal conditions. In most locations, kraft mill effluent will be diluted 20-fold in a rapid manner, and thus would not be acutely lethal to organisms outside a small plume. There are exceptions, such as lethality throughout a one-kilometre bay of Lake Superior, that receives effluent with little opportunity for dilution (Flood et al. 1986). Another exception is the poor dilution available under summer low flow conditions in the Wabigoon River. The river downstream of the mill could run as high as 12% effluent (Beak 1985), which in 1985-86 would mean that it was about 0.5 of the LC50. Still, in a favorable location, the bigger and more general question is not acute lethality, but the large volumes of kraft mill effluent produced and hence the possibilities of sublethal effect over extensive zones.

Species of fish other than rainbow trout are suitable for toxicity tests, since there is no particular evidence that common species of fish differ greatly in their resistance to kraft mill effluent. Guppies are very slightly more sensitive than chinook salmon (Hutchins 1979), and fathead minnows "responded identically" to bluegill sunfish (Zanella et al. 1982). Fathead minnows would also seem to be as sensitive as rainbow trout if we judge through an intermediate organism; fathead minnows were more sensitive than the waterflea *Daphnia magna* in 5 out of 8 comparisons, and the waterflea is similarly less sensitive than trout (following paragraph).

The somewhat lesser sensitivity of *Daphnia* is shown by a summary of work by various researchers (McLeay 1987) which involved 72 comparisons of kraft mill effluent or process streams. The *Daphnia* were more sensitive in only 5 comparisons, the rainbow trout in 27 cases, and there was no appreciable difference in 40 cases. There are opinions that the smaller waterflea *Ceriodaphnia* sp. is more sensitive to lethal effects of pulp mill wastes. That is quite possiblesince it is very sensitive to other effluents (Section 7.3.3).

Other invertebrates, especially aquatic insects, are less sensitive to kraft mill effluent than fish, in the comparisons available (Hutchins 1979). For example, trout were more sensitive than the crustacean *Gammarus*, generally considered a sensitive organism, which in turn was more sensitive than mosquito larvae; trout were also more sensitive than midge larvae when the latter were tested in conditions representing their normal habitat (Fahmy and Lush 1974). Some comparisons between algae and other

organisms are found in the literature but are not particularly valid because lethality in a fish or other animals is compared with the sublethal responses of growth or reproduction of the algae.

8.2 Sublethal Toxicity of Untreated Effluent in Laboratory Tests

SUMMARY. There is a great deal of sublethal toxicological work with aquatic organisms exposed to kraft mill effluent. From these results, we consider that organisms would be protected from overt whole-organism effects if the maximum kraft mill effluent concentration in a waterbody were 0.1 of the LC50 for that effluent, and the average kraft mill effluent concentration were 0.05 of the LC50. That is for discharges without secondary waste treatment. For example, if the LC50 were 30% effluent, the allowable average after dilution would be 0.05 of that, or 1.5% concentration..

By "untreated" we mean effluent that has not received secondary (biological) waste treatment. Primary treatment, standard at Ontario kraft mills, has little influence on acute toxicity.

We have reviewed the literature on sublethal tests, it is extensive, and we do not intend to write out all the details here. Excellent reviews, giving descriptions of background research and tabulation of the results, have been provided by the Canadians Davis (1974, 1976), Kovacs (1986), and McLeay (1987). As an example of the amounts of sublethal data available, McLeay gives 7.5 pages of tables, finely printed with one or two lines per research paper. Kovacs tabulates the findings according to the following headings.

Biochemical metabolites
Blood
Histopathology
Body composition
Respiration and circulation
Growth
Food conversion
Swimming stamina
Early development and reproduction
Behavior

Many of the original papers were seen by us, and we agree in general with the interpretations of all three of the reviewers listed above.

We will generalise from those reviews and tabulations. Many of the sublethal experiments showed thresholds of effect at one-tenth of the lethal concentration (0.1 LC50) or higher, with a few values of 0.05 LC50. Those values corresponded for the most part with concentrations of 1% or 2% whole kraft mill effluent or bleached kraft mill effluent or higher, with an occasional value of 0.5% effluent.

Those are very interesting numbers, because they correspond well with some tried-and-true values which have been used in water pollution work (MOE 1984). If sublethal data are not available for a non-persistent and non-bioaccumulative toxicant, the rule of thumb allows one to estimate that the maximum "safe" concentration at any time or place should not exceed 0.1 LC50, and the average concentration should not exceed 0.05 LC50.

We conclude from this research, most of it under controlled laboratory conditions, that 0.05 LC50 would be a cautious and conservative estimate of allowable average levels in the receiving water, after dilution. As a maximum concentration, 0.1 LC50 would seem to be suitable and again conservative. This is for untreated whole kraft mill effluent, and refers to overt whole-organism toxic effects in aquatic organisms. We believe the allowance to be valid although there are some understudied or missing categories of sublethal research. We are a trifle embarrassed to arrive at these old standard numbers, but they fit, and others have arrived at similar values (reviewed in Brouzes 1976). We are aware of more objective mathematical methods of arriving at water quality criteria (Stephan et al. 1985) but do not feel that they would reach more valid estimate.

Another generalisation has been made by Kovacs (1986) from his tabulation of sublethal research. The lowest concentrations (most sensitive effects) tend to be associated with internal physiological changes, not with whole-organism effects. As discussed elsewhere (Section 7.2.2) the latter category is the important one for evaluating meaningful damage to aquatic organisms. Perhaps we may give one example of the necessity of avoiding an interpretation that any biochemical change within a fish is a deleterious effect, but instead, the need to verify damage with some measure of performance or well-being of the whole fish. McLeay and Brown (1974) exposed small coho salmon to neutralised bleached kraft mill effluent for 200 days, which would qualify as a sub-chronic exposure, if not a chronic one. They had clean-water control fish, and fish exposed continuously to 0.1 LC50, and others to 0.25 LC50. Both groups of fish exposed to bleached kraft mill effluent showed the following biochemical symptoms:

decrease in blood serum pyruvate levels;
increase in the ratio of serum lactic acid to pyruvic acid;
elevation in plasma glucose levels; and
increase in the liver-muscle ratio of glycogen.

At the higher but not the lower concentration, there were additional symptoms:

elevated lactate levels in the blood and muscle; and
decrease in body protein content.

Certainly those things sound as if they should be deleterious, and the researchers concluded in general that the exposed fish had developed an oxygen debt (the result of insufficient oxygen supply to the tissues). However they also measured growth of the fish, which had all started out at the same weight of 1.3 g. After the 200 days, control fish averaged 12 g in weight, those from the low concentration were 15 g, and those from the high concentration were 23 g, almost twice as big as the control fish. The authors were unable to explain this result, but it was apparent that the whole-organism performance was better in these low concentrations of effluent. That is what counts, particularly performance as measured by growth and reproductive success.

Since the Canadian review articles were compiled, there has been an upsurge of sophisticated biochemical-physiological research on fish exposed to kraft mill effluent or its components, much of the work from Scandinavia (e.g. Andersson et al. 1987, Oikari and Kunnamo-Ojala 1987, and Tana and Nikunen 1986b). This recent work is specifically reviewed by Andersson (1987). The research does not result in any lowering of estimated "safe" levels. It does, however, show some biochemical and physiological disturbances within fish at astonishing distances from pulp mills (see Section 9.6), and the researchers feel that several of the changes will be useful as sensitive tests for deleterious sublethal exposure of wild organisms.

One apparent gap in the sublethal toxicity studies with untreated kraft mill effluent is published information about the effects on reproduction of aquatic organisms. The most sensitive and convincing evaluation of sublethal effect for most toxic compounds is generally a life-cycle exposure, with particular attention to (a) reproductive success of the first generation, and (b) survival and initial development of the second generation (see Section 7.2.2). There may be many such tests carried out under the US permit program, using reproduction of *Ceriodaphnia* sp., but of course they are not available in the scientific literature, nor even in report series. Recent US tests on pulp mill effluents would in any case be on treated effluents for the most part.

There are life-cycle tests for biologically treated waste in the accessible literature, but none were found for untreated kraft mill effluent, despite the plethora of other sublethal tests, and there are only a few pieces of research dealing in any way with reproduction or young stages. Those pieces of information do not cause a major change in our estimated water quality criterion. For example, eggs of the tropical zebrafish showed reduced hatching after the parents had been exposed to 0.03 LC50 of bleached plant effluent, but that would be more toxic than whole bleached kraft mill effluent (IPK 1982). We have depended on the other types of experiments for sublethal effects.

8.3 Avoidance Reactions by Fish

SUMMARY Fish show weak avoidance, or no avoidance, of low concentrations of kraft mill effluent, although they may avoid lethal concentrations. Accordingly they might remain in a polluted habitat and suffer sublethal damage, or they might be caught by a lethal spill. However, it is not likely that harmless low levels of kraft mill effluent would cause fish to abandon a favorable habitat.

There has been relatively few study of whether fish will avoid pulp mill waste, and that is unfortunate since such behavioral reactions to a pollutant do not necessarily correspond to actual physiological damage caused by that pollutant. Most of the available research indicates that fish do not show particularly strong avoidance reactions to kraft mill effluent. On the one hand, that could be dangerous, since fish might fail to move out of polluted areas and would suffer whatever sublethal effects were caused by the effluent. In the extreme case of a severe spill, there might be a massive kill because fish did not react quickly enough to move away from a plume and into a tributary or other haven. On the other hand, this lack of avoidance could be beneficial, given a non-toxic mill effluent and no accidental spills; fish populations would apparently not be chased out of suitable habitat just because it had harmless low concentrations of kraft mill effluent.

Laboratory experiments with kraft mill effluent in fresh water show that consistent and strong avoidance reactions by juvenile salmonids occur only at relatively high concentrations of 2 - 30% effluent, or at lethal concentrations (Jones et al. 1956, Gordon and McLeay 1978). At low concentrations reactions are weak (Sprague and Drury 1969) or fish may be attracted to the effluent, whether it has been treated or not (Gordon and McLeay 1978).

There has been few field studies on avoidance, because it is very difficult to carry out. The few observations on fish exposed to a plume of real effluent support the lab findings, i.e. a weak avoidance reaction or none. A decade ago, eight fish were tracked by electronic tags after release near the mill at Red Rock. The tracks of the fish suggested avoidance reactions to effluent concentration below 15%, but netting indicated that the highest numbers of fish in Nipigon Bay were congregated within 1 km of the mill

(Kelso 1977). Jones et al. (1956) give an anecdotal account of fish showing signs of asphyxiation in high concentrations of kraft mill effluent, in a stream where avoidance reactions should have been possible. Similar observations of weak to moderate avoidance, difficult to interpret objectively, have been recorded in estuaries (e.g. Elson et al. 1972). A few other pieces of research with similar conclusions are reviewed by McLeay (1987, p. 55 and 95).

8.4 Tainting of Fish (and Water)

SUMMARY. (1) Kraft mill effluent can cause off-flavours in fish at concentrations in the vicinity of 1%. In some cases that represents tainting thresholds at 0.1 or 0.2 of the LC50, approximately equal to the lower range of concentrations causing sublethal effects on fish. Tainting of fish by kraft mill effluent has had small effects on both recreational and commercial fishing in Ontario. (2) Condensates are important sources of tainting chemicals in mill effluent, but the bleach plant is not. (3) Treated kraft mill effluent can taint very pure drinking water at fractions of 1% concentration, but more normal surface waters may require higher concentrations. However those are thresholds, and some city tap-water may have stronger taste or odour (e.g. Montreal). (4) Secondary waste treatment of kraft mill effluent reduces tainting by a factor of about 10, for either fish or drinking water, and aeration also decreases fish taint.

Tainting is an important topic, not so much for the self-regard of the fish as for potential human consumers. It has been of some economic importance in Ontario, and in the classic survey of the Spanish River (Dymond and Delaporte 1952) a taste panel reported that pickerel had "an objectionable bad taste", a conclusion already evident to local people who wished to use the resource. More recently, commercial fishing catches from Nipigon Bay have been periodically rejected for sale because of off-flavour, although the fish themselves seemed to congregate happily in the vicinity of the mill (Kelso et al. 1977).

We have consulted the original literature but for detailed numbers and references we refer the reader to existing good reviews with Canadian points of view (Brouzes 1976, Kovacs 1986, McLeay 1987). A more general review with extensive listing of taint-causing chemicals has been provided by Persson (1984).

Not all results of research on tainting need be taken at face value. It is technically difficult and relatively subjective to measure off-flavours, and "amateurs" have sometimes attempted such work with unreliable results. For example, one technique known as the "hedonic" method involves rating the flavour on a numerical scale, for a set of unreplicated samples with one hidden control and one identified control; the method can give undependable results but is in the literature. Also there are many natural substances which may produce off-flavours in water and in fish. Finally, in a result that tends to shake our faith in statistical testing, it has been scientifically and statistically documented by excellent procedures, that when exposed to foul condensate of a kraft mill, rainbow trout pick up more taint on their left side than on their right side (Liem and Naish 1979)!

Effective concentrations for fish. Tainting by untreated whole kraft mill effluent occurs at concentrations similar to those causing sublethal effects on the fish. (There is no evidence that the tainting itself harms the fish's performance.) Exposures in the laboratory estimate tainting thresholds of untreated bleached kraft mill effluent that are generally in the 1% to 5% range, with some estimates down as low as the region of 0.5% (Shumway and Chadwick 1971, Cook et al. 1973, Liem et al. 1977, Whittle and Flood 1977, Gordon et al. 1980). This would correspond, in two cases at least, to 0.12 LC50 and 0.2 LC50, or down at concentrations near the limit for sublethal physiological effect (Whittle and Flood 1977, Cook et al. 1973).

There have been field studies on the taste of fish caught in various locations, or held in cages. The studies confirm that tainting does occur, and give some general confirmation of the concentrations listed above, but do not add greatly to the precision of the estimate. Usually the results are expressed not in terms of kraft mill effluent concentration, but as distance of the fish's location from the mill, and often even that information is missing. Some sets of results appear to be confounded with natural off-flavours. Studies on taste of marine shellfish are not considered here.

Sources and treatment. Condensates from recovery furnace flue gas (Cook et al. 1973), digesters, and multiple-effect evaporators are known sources, estimated to contribute 20% of tainting properties of a bleached kraft mill (Blackwell et al. 1979). Naish and Brouzes (1980) concluded that the recovery area contributes most of the tainting substances from a mill. Although those sources produce many strong-smelling chemicals such as mercaptans and sulfides, it is not documented that they cause the off-flavour in fish.

Bleaching apparently does not contribute significantly to tainting, and in particular, recent opinion is that chlorinated phenolics do not have an effect (Kovacs et al. 1984).

Secondary waste treatment greatly reduces the tainting problem, as does aeration (Cook et al. 1973). Biological treatment of bleached kraft mill effluent resulted in a 4 to 10-fold drop in tainting (Gordon et al. 1980), and about a 2-fold drop (Miettinen et al. 1982).

Drinking water Many people in Ontario have groundwater as a domestic supply, but many others use surface water. Often the surface water is relatively clean, even before treatment at the intake, but some municipalities must use lake or river water that has received industrial waste such as pulp mill effluent.

Very pure drinking water may suffer impairment of taste and odour with the addition of as little as 0.1% to 0.4% of biologically treated bleached kraft mill effluent. For untreated bleached kraft mill effluent, the threshold was about an order of magnitude lower (Kovacs and Voss 1986). However those concentrations are to some extent unrealistically low for most human consumers. The tests were very sensitive ones with glacier-fed water as the background "drinking water". Montreal city tap-water was included in the tests as a standard, and it was rated (by the taste panel of Montreal residents) as having almost as much odour as 2% bleached kraft mill effluent in the glacier water, and almost as much taste as 0.5% bleached kraft mill effluent!

In tests with water from four rivers that received biotreated bleached kraft mill effluent, the lowest concentrations detected as having a taste or odour problem were 0.4%, 0.6%, >1.0%, and 2.1%. Again, however, Montreal tap-water was included in each comparison, and it had the strongest taste or odour in each of the four cases, although bleached kraft mill effluent concentrations ran up to 3% in some tests (Wong et al. 1985).

We think that the lowest thresholds listed above should not be accepted as applying without qualification to all potential surface drinking water. Problems could exist in cases of very clear, soft water and Lake Superior comes to mind. We have not investigated public opinion in such places as Terrace Bay, where the lake provides tap water and receives bleached kraft mill effluent, since any problems of this nature would be obvious to residents, and should generate demand for a cure. It is worth pointing out that tainting of water is, on the strength of one reference, much worse for untreated waste. Therefore secondary treatment of mill effluent is a clear option to solve any problem, although it does not completely eliminate tainting of water (Kovacs and Voss 1986).

8.5 Mutagenicity

SUMMARY. (1) There are mutagenic chemicals in kraft mill effluent. The most important source is chlorination effluent from the bleach plant. Several of the specific chemicals have been identified, and they are various chlorinated low-molecular-weight organic substances. These mutagens do not appear to be strongly persistent in the environment. (2) Substitution of chlorine dioxide for chlorine can reduce or eliminate the mutagens. They tend to decompose at neutral pH, and disappear quickly in strongly alkaline conditions. Secondary waste treatment is the other option for removing mutagens from discharges. (3) Eliminating mutagens is not necessarily the same thing as eliminating carcinogens. Some carcinogens are not mutagens and so would not be detected by the Ames test or by other screening tests, as pointed out in Section 10.8.8 on dioxins. (4) Japanese researchers have found one location where pulp mill wastes seem to be associated with neoplasms in fish.

In recent years a number of rapid tests have become available, which use micro-organisms or cell cultures in screening the mutagenic (genotoxic) potential of substances. The tests have been heavily used, since a mutagenic substance may also be a carcinogenic one. However, that always has to be documented, and the list of confirmed carcinogens is smaller than might be thought. Similarly, some carcinogens are not mutagens, e.g. "dioxin" as explained in Section 10.4. In any case, the mutagenicity tests have been used on kraft mill effluent and its components. The recent Canadian reviews do not appear to have covered the topic, although Stockman et al. reviewed it some years ago (1980).

Commonly used tests are: (a) the *Ames* test using back-mutation in the bacterium *Salmonella typhimurium*; (b) increased frequency of sister chromatid exchange *(SCE)* using ovary cells from Chinese hamster; (c) *DNA repair* in the intestinal bacterium *Escherichia coli*; and (d) the so-called *Rec assay* to measure DNA damage using *Bacillus subtilis*. The various tests often yield somewhat different answers, presumably because of differing modes of activity of different chemicals.

Whole bleached kraft mill effluent (without secondary treatment) has usually been found to be weakly mutagenic (B.C. Research 1979, Höglund et al. 1979, Langi and Priha 1987).

The first chlorination effluent has generally been found to be the strongly mutagenic component of mill waste, but the caustic extraction effluent does not carry mutagens (Fevolden and Moller 1978, B.C. Research, 1979, Eriksson et al. 1979, Höglund et al. 1979, Nazar and Rapson 1980, Rannug et al. 1981, Langi and Priha 1987). In one case, E-stage effluent was positive with SCE but not with the Ames test (Langi and Priha 1987).

Absence of mutagens in the E-stage is apparently because they are sensitive to alkaline conditions. The mutagens in chlorination effluents, at pH 1.8 and 6°C, retained their activity for a year. At pH 7 and 20°C, two weeks was enough to lose 90% of the mutagenicity, while at pH 10 it was gone in a few hours (Eriksson et al. 1979).

Removal of the mutagens from an effluent can be done with secondary waste treatment. Aerated lagoons remove most or all (B.C. Research 1979, Höglund et al. 1979). Mutagenicity of lagoon discharge was found in one case, with SCE but not with the Ames test, while activated sludge effluent at a similar mill was negative on both tests (Langi and Priha 1987).

Substitution of chlorine dioxide for chlorine is very effective. In experiments with softwood pulp, strong mutagenicity of chlorine dropped off linearly with substitution, until at 100% ClO_2, mutants were no greater

than in the control (Eriksson et al. 1979, Nazar and Rapson 1980). Rannug et al. (1981) also found no mutagenicity of material from a chlorine dioxide stage.

Nor does a hypochlorite stage have mutagenicity (Eriksson et al. 1979), although it could be demonstrated by concentrating that kind of effluent (Rannug et al. 1981).

Sulfur dioxide treatment also eliminates mutagens in mill effluents. This can be done in a few minutes treatment with gaseous SO_2 (B.C. Research 1979, Donnini 1981).

Some specific mutagenic chemicals have been isolated from chlorination effluents and identified. Two of those listed below were identified as high-activity components by Kringstad et al. (1981). Workers at Paprican were able to extract 70% to 90% of the mutagens with ethyl acetate (Holmbom et al. 1981, 1984). They discovered a new chemical that is a major contributor of the mutagenicity of chlorination effluent and behaves similarly, for example it disappeared quickly in alkaline pH. (The chemical is 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone, or for short, trichlorohydroxyfuranone, a single-ring molecule with an oxygen in the ring, which carries various substituents including chlorine .) Holmbom et al. (1984) list the following mutagens identified from the chlorination stage.

trichlorohydroxyfuranone
2-chloropropenal
1,3-dichloroacetone
1,1,3-trichloroacetone
1,1,3,3-tetrachloroacetone

A detailed tabulation of individual chemicals with test-data on carcinogenicity and mutagenicity is given by Beak (1987, Appendix 8). Beak reports that of 128 chemicals for which there is one or other positive finding for genotoxicity, only 52 have been found in pulp mill effluent. That proportion does not sound reassuring, but the tabulation included such categories as "suspected mutagens", and in fact only two "confirmed carcinogens" have been documented in mill waste (arsenic and benzene). Two chlorinated compounds were among the "candidate carcinogens" (chloroform and 2,4,6-trichlorophenol).

Field observations on this topic are notable for their rarity, but some Japanese researchers have attempted to establish cause and effect at a coastal location (Kinae et al. 1981a, b). Descriptions of the work are rather sketchy, for example three pulp mills were assessed but mill processes were not specified. Nevertheless, it appears that half of the spotted sea trout near mill S had a skin neoplasm called melanoma. Extracts from the sediments near mill S were mutagenic by two tests, but the other two sediments were negative or positive in only one test. From the mill S sediment, 28 organic compounds were extracted, several of them known as components of kraft mill effluent. Two of them were mutagenic (2,4,6-trichlorophenol and 3,4,5,6-tetrachloroguaiacol). Fish were caught from the 3 locations, and liver extracts were mutagenic for the fish from mill S only. Extractions from the fish obtained 18 organic compounds of which 12 were the same as obtained from the sediment.

These mutagens have been diagnosed as relatively non-persistent in the environment by Höglund et al. (1979), because they are biodegradable and easily metabolised by certain components taken from rat livers. The Japanese work seems to be the only report that could indicate persistent mutagens from a pulp mill. As mentioned, the published papers are so sketchy in description of the work, that its significance and validity is therefore difficult to assess. However, twice in the last couple of decades, Japanese coastal areas have given the rest of the world early warnings about issues of environmental and

human health, and we do not dismiss the possibility of an association between pulp mill wastes and neoplasms in fish.

8.6 Ecosystem and Field Assessments with Kraft Mill Effluent

SUMMARY. (1) Some North American research in small artificial ecosystems and in the field gives confirmation that unbleached kraft mill effluent concentrations of 0.05 LC50 do not cause observable sublethal effects in fish. (2) Some field surveys cannot be used to assess toxicity as a separate item, because the effects of low oxygen and settling solids are also included in the assessment. Some mills discharging into Lake Superior have a restricted zone of damage of the order of 1 km^2 or less. One with a diffuser had a small area of 0.12 km^2 within which the effluent concentration was greater than 1%, and effects were scarcely detectable, even though the effluent failed the monitoring test for trout lethality.

General confirmation of the toxic concentrations found in lab work has been provided by a few experiments in small artificial ecosystems. Artificial streams have been used at Oregon State University for a number of years with interesting results. In one set of experiments, small chinook salmon were stocked in the artificial streams, and had to find their food from the invertebrates living on the bottom, during trials that lasted one to four months (Seim et al. 1977). One of the trials showed that unbleached, untreated kraft mill effluent reduced salmon growth at 0.2 LC50 but not at 0.07 LC50 (1.5% and 0.5% effluent). Another trial showed that similar levels of 0.05 and 0.09 LC50 were not only apparently harmless, but actually boosted production of both fish and invertebrates, as seen in Table 8.2 .

Table 8.2 Growth and production of aquatic organisms in artificial streams dosed with unbleached kraft mill effluent. Data from Seim et al (1977).

	Average weight of salmon at end of test, grams	Weight of invertebrates in grams per square metre of stream bottom
Control water	2.1	1.7
Control water	3.0	1.6
Treated KME, 1.5%	2.1	1.8
Treated KME, 7.5%	3.5	1.4
KME, 0.05 LC50 (0.75%)	5.3	2.9
KME, 0.09 LC50 (1.5%)	6.6	2.6

Clearly the kraft mill effluent added nutrients that improved productivity of the artificial streams, and the untreated waste did that more successfully.

8.6.1 Field Studies in Lake Superior

There are numerous field surveys around mills including Ontario kraft mills. In some cases it is difficult to draw any conclusions about sublethal toxicity *per se*, because if present, toxic effects are confounded with effects of reduced oxygen and deposition of fibres. In some cases simple colour has an effect because it reduces photosynthetic activity, and hence populations of algae. One of the most thorough field studies was the multi-facetted investigation in Nipigon Bay in 1974, with respect to the mill at Red Rock. Dilution of the mill effluent was rapid, and the area of lake exposed to concentrations greater than 1% was estimated as 1.5 km^2. Within that area, only 0.5 km^2 (700 m x 700 m) suffered "severe ecosystem disruption" (Kelso et al. 1977). Part of that may have been from toxicity, which could be interpreted as validation of laboratory findings, since the ecosystem disruption would have been associated with concentrations greater than 1%. There were effects going much further, notably slight elevations in bacterial populations at distances up to 19 km (Rokosh et al. 1977), presumably in response to elevated nutrients. Bottom-living invertebrates also changed over many km, but for factors other than toxicity (Vander Wal 1977). Fish, on the other hand, were more numerous near the mill than away from it (Kelso 1977). It should be noted that the mill at Red Rock is largely unbleached kraft (as of 1986, 75% unbleached kraft, 20% groundwood, and 5% bleached kraft).

Another field study showed an even smaller zone of influence, for direct discharge to Lake Superior using a diffuser (Craig et al. 1986). Dye-tests showed that a dilution of 1% was achieved within an area of 0.12 km^2, which, for example, could be represented by a rectangle 120 m by 1000 m. Dilution to 0.1% was achieved about 4 km down-plume. No lethality of trout was measured when they were held in cages directly in upwelling plumes from the diffuser. Trial netting showed similar kinds and numbers of fish directly in the plume and at a control location, with lake trout and lake whitefish included. There seemed to be small effects on the bottom-living invertebrates at 38 m from the diffuser (scarcely surprising) but even at such close-in locations there were larger numbers of a sensitive crustacean ("freshwater shrimp"), apparently attracted by alga.

In the study by Craig and colleagues, the effluent could be detected by slight chemical changes, for samples taken right in the plume near the diffuser. For example the pH dropped only from 7.5 to 7.0, colour increased from 4 to 42, and BOD rose to only 7.2 mg/L compared to values of 0 - 4 that may be found in clean water. Those changes are small values are the worst recorded, and apply to the closest-in sample at the deepest point near the diffuser. No appreciable effect was detected on dissolved oxygen concentrations in the lake.

The apparent lack of appreciable environmental effects at this mill discharging directly to Lake Superior is thought-provoking, since the effluent was lethal to rainbow trout at 25% concentration. Apparently a mill can fail the fish toxicity test without necessarily causing overt damage, given enough dilution water. Whether there were more subtle effects such as bioaccumulation of toxicants or damage by persistent organochlorines, was not addressed in the report.

Such favorable situations do not always apply. Another discharge to Lake Superior enters at the end of a small bay where there is poor dispersion. The result is an area of about 1 km^2 in that bay which has lethal conditions for fish (Beak 1986Y).

Recent Swedish field and ecosystem studies are covered in Section 9.6 of this report. Some field studies near a bleached kraft mill indicated effects on fish at effluent concentrations of 0.1%. That represented about 0.004 LC50, an order of magnitude lower than our suggestion for an acceptable concentration. We

are uncertain about the relevance of the Swedish concentrations, since they may represent combined action with pollutants from other sources around the Baltic Sea, which is suffering severe problems with persistent toxicants. Accordingly we will stick with our estimate of 0.05 LC50 as a long-term acceptable concentration.

8.7 Effects of Biotreated Effluents

Well-treated kraft mill effluent is only mildly toxic, according to numerous papers and reports. To pick a striking example, an earthen effluent channel receiving biotreated bleached kraft mill effluent from a Florida mill was home to 25 species of fish, 4 of them common, and bottom-living invertebrates (midge larvae) averaged about 6,000/m^2 (Juul and Shireman 1978). We will document some items on effects of treated waste that are relevant to the Ontario situation.

Acute lethal action of treated effluent has already been described in Section 8.1. It was shown that biotreatment did not necessarily make effluents non-lethal. Discussion of procedures necessary to make treatment perform satisfactorily is given in Section 5. We point out that if secondary treatment is not satisfactorily removing acute lethality, then it will not be reducing the sublethal effects either, and the comments below about relatively high concentrations to cause sublethal effects will not be relevant.

Sublethal effects may occur only at high concentrations of 10% or more. The list below summarises the summary of McLeay (1987), for research on chronic sublethal toxicity of biotreated bleached and unbleached kraft mill effluent, in laboratory and artificial ecosystem tests. Listed after each category of effect are the concentrations, as %, found by various investigators to cause an effect.

Internal physiological effect	<5, <5
Respiration, circulation	>1, >2, >10, >10
Swimming performance	>1, >28
Feeding behavior	>5
Tissue abnormalities	1, >1, >2, >4
Growth, development	>4, 5, >5, 10, 10, 32, >100
Disease resistance	<1, >2
Reproduction or young stages	1.3, <4, >7, >100
Productivity, lab or outdoor streams	1.5, >2, <4

Only one value is less than 1%, and that was a legitimate finding of increased gill parasites in exposed fish (Lehtinen and Oikari 1980). One of the most sensitive tests is known to be one for abnormal development of oyster larvae, and that gave rise to the value of 1.3% for a reproductive effect (Woelke et al. 1972). All the other findings are for fish, except the two values >100 which are for lack of effect of full-strength effluent on the waterflea Daphnia, in life-cycle exposures (Weinbauer and Somers, 1982). It is reassuring to have some results for invertebrates, since removal of toxicity to fish does not necessarily mean removal for invertebrates (Sprague and McLeese 1968). Algal production may be stimulated by treated kraft mill effluent at concentrations up to 5% or even 25% (Bothwell and Stockner 1980).

The above list of effect concentration includes several pieces of research on reproduction, young stages, and stream ecosystems, all of which yield meaningful whole-organism assessments, and convey an impression of reliability when read in the original.

Thus it appears that a well-treated effluent would cause overt sublethal effects only at concentrations of 1% or more. The size of affected areas would be extremely small given favorable dilution such as those described in Section 8.6.

8.8 Toxicity Sources: Relative Importance and Joint Action

SUMMARY. (1) The most important sources of toxicity (as measured by lethality to fish) are often leaks and minor spills, brownstock washing, both bleach plant streams, and blow heat condensate. Potential remedies are better control of the processes, neutralisation of waste, or biological treatment. (2) The toxicity of a combined effluent is usually found to be somewhat less than the sum of the individual toxicities of its component streams. The evaluation must be done in terms of amount of toxicity, measured as toxic units multiplied by rate of flow.

Preceding parts of this chapter considered whole effluent. The following sections will examine the kinds of toxic effects caused by some of the individual sources and components of waste. This part intends to describe:

the relative amounts of toxicity contributed by various streams within the mill; and
whether or not the toxicity of the whole effluent is approximately the sum of its parts.

The only reasonable way to approach those questions is to compare, not the lethal concentrations of various streams, but the amounts of toxic material, taking into account the volume of flow of each stream. The measuring scale is as follows.

$$\text{Toxic Units (TU)} = \frac{100\%}{\text{LC50 as \%}}$$

Toxicity Emission Rate = TER = TU x (volume of flow in m3/day)

A further refinement allows comparison between mills by expressing the amount of toxicity in terms of production, i.e. air-dried tonnes of pulp.

Toxicity Emission Factor = TEF = TU x (volume of flow in m3/tonne of pulp)

For one Ontario bleached kraft mill, Scroggins (1986) reports the toxicity balances shown in Figure 8.1. The toxic units are based on standard rainbow trout lethal tests.

The pulp mill sewer was the biggest of the three sources, as is evident in Figure 8.1. Scroggins rated the most important sources, per tonne of pulp, in the order shown below. The sewer that collected each waste is indicated in parentheses.

Washing and screening	(pulp mill sewer)
Blow heat accumulator	(condensate sewer)
Bleach plant, particularly extraction stages	(acid and pulp mill sewers)
Woodroom	(pulp mill sewer)

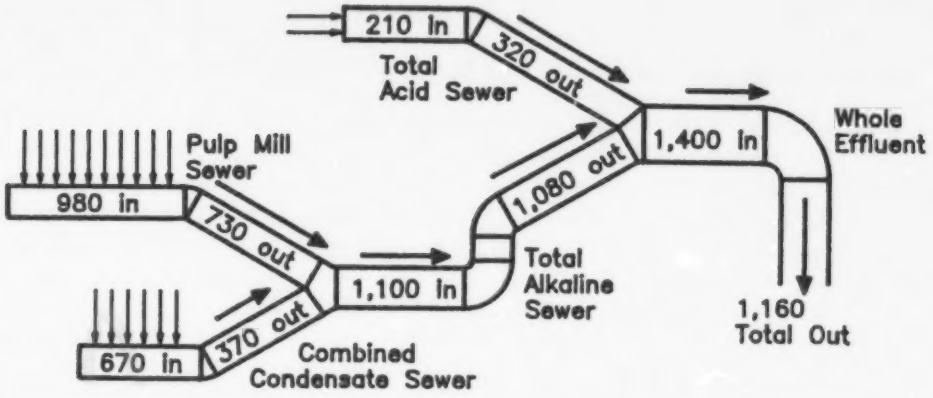

Figure 8.1 Toxicity balance for a bleach kraft mill. The numbers represent "Toxicity Emission Factors" (TEF) in terms of Toxic Units, times cubic metres of effluent, per tonne of pulp produced (see text). The arrows on the left represent various individual streams which combine into a sewer. Their individual toxicities were measured, individual TEFs were calculated, then the TEFs were added together to yield the values shown outside and just to the left of the boxes . The numbers going "in" are the sums of individual measured values of TEF. Those going "out" are measured, and provide the component to be added for the next "in" (Data from Scroggins 1986)

That tabulation of sources is somewhat generalised from Scroggins' list, since there were actually two mills within the total operation. The bleach plant extraction effluent from one mill went to the pulp mill sewer while the same effluent from the other mill went to the acid sewer. Both were operating on softwood for the evaluation shown above. The important conclusions from the study, insofar as reducing toxicity of the effluent, were the recommended control procedures. The two most important improvements were the following.

1. Decrease the spills of black liquor.
2. Provide countercurrent recycle of the brown stock washers.

The degree of combined action shown by Fig. 8.1 is typical of that found by most investigators, i.e. that toxicities of the various streams either act in a manner that approximates additivity, or else they are less-than-additive (Bruynesteyn 1977). Less-than-additive is shown by many of the boxes in Fig.8.1, for which the sum of the individual TEFs of the incoming streams is greater than the actual measured TEF of the new combined stream. For example, in the upper left of the diagram, 10 streams combine and the sum of their individual toxicities is 980, but only 730 was measured. A more-than-additive effect (lower left) is not usual and in this case is probably a pH effect.

Another study in a nearby bleached kraft mill showed somewhat similar results. Craig et al. (1986 Table 4.9) concluded that the largest items in the toxicity balance were as follows (with estimated TEFs in parentheses).

Spills and leaks	(170)
Alkaline sewer (bleach plant)	(165)
Acid sewer (bleach plant)	(135)
Blow heat condensate	(61)
Brownstock washing	(43)

In the study by Craig and colleagues, the sum of the toxicities of individual streams going to the clarifier (everything except the bleach plant streams) was estimated as 310, but that did not account for the measured TEF of 520. However when the clarifier output (415) was added to the TEFs of the two bleaching wastes, the total was reasonably close to the measured total output of the mill, which averaged 610 TEF.

8.9 Major Toxic Components of Kraft Mill Effluents

In this section we are concerned with the non-volatile toxicants within the mill. Although appreciable toxicity may result from volatile substances (sulfides, mercaptans, and sulfur dioxide) those things are so easily prevented from reaching surface waters that they are not considered here. Similarly an unfavorable pH may account for considerable toxicity of an effluent (Howard and Walden 1965) but that also is a relatively straightforward item to remedy, and in any case, the pH will usually reach that of the receiving water be fairly quickly by dilution.

For the non-volatile toxicants remaining, we may generalise as in Table 8.3, from findings on acute lethality according to the classic work of Leach and Thakore (1973, 1977), supplemented by information from McKague (1981) and Walden and Howard (1977).

The list is imposing, but has some repetition. The major items seem to be resin acids and fatty acids, diterpenes, pitch dispersants, and a range of chlorinated substances including lignins, phenolics, and again resin and fatty acids. The toxicity of these will be discussed to some extent below, with chlorinated organics being taken as one category.

Table 8.3 Principal toxic constituents of kraft mill effluent streams. Sub-items are listed in approximate order of prominence.

Effluent stream	Major toxic contributors	Lesser toxic contributors
Debarking	Resin acids Isopimaric Dehydroabietic Abietic Pimaric	Diterpene alcohols Pimarol Isopimarol Dehydroabietal
Pulping (unbleached whitewater)	Sodium salts of resin acids Na isopimarate Na abietate Na dehydroabietate Na pimarate	Sodium salts of unsaturated fatty acids Palmitoleic Oleic Linoleic
Acid chlorination	Chlorolignins 4,5-Dichlorocatechol 3,4,5-Trichlorocatechol Tetrachlorocatechol 2,6-Dichlorohydroquinone	?
Caustic extraction	Chlorinated stearic acids Epoxystearic acid Dichlorostearic acid Chlorinated resin acids Monochlorodehydroabietic a. Dichlorodehydroabietic a. Chlorinated phenolics Tetrachloroguaiacol Trichloroguaiacol	Liquid pitch dispersants

8.9.1 Resin Acids and Fatty Acids (RFA)

SUMMARY (1) Resin acids in kraft mill effluents contribute a major proportion of the acute lethality that may show up in the toxicity monitoring. However these substances decompose fairly readily and do not pose a big problem of persistent toxicity. Fatty acids contribute a smaller amount of toxicity, and they also decompose. (2) Toxicity from escaping resin and fatty acids is most efficiently controlled within the whole-effluent toxicity monitoring test with rainbow trout. If toxicity is not acceptable, the contribution by resin and fatty acids may be decreased by improving within-mill procedures or by secondary waste treatment.

The Ministry has recently obtained a criterion document for resin acids, which includes a thick and thorough consideration of information available in the scientific literature (Taylor and Yeager 1987).

From tests of acute lethality, it has been recognised since the 1930s that resin acids were responsible for a large proportion of the toxicity of pulp mill waste. Bergström and Vallin (1937) concluded that one stream from the mill contained most of the waste resin acids and was responsible for "95% of the total poisonous effect" of mill waste on small salmon. Half a century later, it is still true that resin acids contribute much of the acute lethal action of untreated kraft mill effluent. The sodium salts of resin acids contributed 80% of the toxicity of the whitewater from kraft pulping, and sodium salts of unsaturated fatty acids contributed the rest, in a study by Leach and Thakore (1973).

An astonishing total of 41 estimations of the lethal concentrations for fish, have been made for seven resin acids, and they are all quite similar, the extreme values being 0.2 and 2 mg/L (Taylor and Yeager 1987). These substances lose toxicity in alkaline water, and become more toxic in acid water; in view of their importance in kraft mill effluent, it would be most realistic to carry out any monitoring toxicity tests at the pH of the receiving water, or at neutral pH.

At sublethal concentrations, resin acids do not have any single clear-cut mode of action, but rather a whole suite of effects on blood, respiratory capacity, liver functioning particularly the management of energy exchanges, and enzymes. There does not appear to be definitive useful information on the concentrations deleterious at the whole-organism level.

Well-operated secondary waste treatment readily degrades resin and fatty acids. McLeay (1987) estimates about 90% disappearance for resin acids and about 70% for fatty acids. Beak (1987) cites an example of an Ontario mill with an aerated lagoon which reduced resin acids in the effluent by more than 96%, and fatty acids by more than 99%. Individual chemicals were assigned mean values for percentage removal in biological treatment, ranging from 65% to 97% for resin acids, and from 71% to 100% for fatty acids (Beak 1987, Table 8.1).

RFA are not great travellers in the environment, as might be expected from their biodegradability. In a lake in Finland which received treated bleached kraft mill effluent, Oikari et al.(1985a) compared water concentrations only 0.8 km away with those 0.1 km from the mill. For four prominent resin acids, there had been an average disappearance of 97%, and for three prominent fatty acids, the disappearance was 90%. Detectable amounts of resin acids could be found in the blood plasma and bile of rainbow trout held

for a few days in cages at 0.8 km, and closer in, the concentration factors of plasma over water were 40 to 60 times.

Upon chlorination, some of the RFA are oxidised, while others form chlorinated compounds that are much more persistent. We deal with this and other chlorinated toxicants in Section 9.

Taylor and Yeager (1987) present a case for using water quality criteria for regulation of total resin acid, and dehyroabietic acid (DHA) specifically. We do not support such a case because "resin acids are nearly insoluble in water" (Taylor and Yeager 1987), and therefore travel with particles or organic matter. Taylor and Yeager further suggest regulation of DHA as persistent and bioaccumulative substance. We do not agree with that either, considering that the same authors describe a half-life of only six weeks for DHA in Lake Superior water. DHA is taken up by fish, but it also disappears from them when they are removed from the source, so we do not regard it as a dangerous bioaccumulative substance.

To control the effects of RFA in kraft mill effluents, we do not suggest any attempt to regulate their amounts or concentrations by chemical measurement and monitoring. Since RFA are among the larger contributors of acute lethality of effluents, and since the non-chlorinated forms cannot be considered to be persistent toxicants, we recommend assessing them along with other acute toxicants, by use of the general fish toxicity test on the whole effluent (i.e. lethality, see Section 7.3). If the RFA are major contributors of acute lethal toxicity in a mill's effluent, the control options would be improved processes within the mill so that a greater proportion reaches the recovery furnace or secondary waste treatment.

8.9.2 Diterpenes

Neutral diterpenes including alcohols, aldehydes, and ketones have been shown to contribute appreciable acute toxicity in bleached kraft mill effluent. Those that collected in the foam of a lagoon contributed 30% of its toxicity, the remainder being caused by resin acids (Servizi et al. 1976).

8.10 Factors Modifying Toxicity

SUMMARY. (1) Kraft mill effluent is more toxic at low pH, and therefore in toxicity tests for monitoring effluents, the pH should be standardised either at neutrality or at the natural pH of the receiving water. (2) Low dissolved oxygen and kraft mill effluent toxicity interact to increase the effect of each other. It is important to maintain reasonable concentrations of dissolved oxygen in the receiving water, not only because of the deleterious effects of low oxygen, but also because of the interaction with toxicity.

Two major conditions of the water can change the acute toxicity of kraft effluent, and these are pH and low dissolved oxygen concentration.

As pH rises, bleached kraft mill effluent loses toxicity, and a change from pH 6.5 to 8.5 could result in a toxicity decrease of one half (McLeay et al. 1979). The change seems to result mainly from the ionisation of resin acids at high pH, and a resulting decrease in toxicity compared to the unionised forms. Presumably the sublethal effects would change in a similar fashion. Thus the toxicity of kraft mill effluent could vary in natural waters since they can have different pH values, for example pH 6.5 in very soft water, and greater than pH 8 in very hard water.

The influence of pH makes it important to standardise that characteristic in toxicity tests. Bleached kraft mill effluent varies in pH from mill to mill but can be very acidic. Aside from any toxicity of the low pH itself, this would make the toxicity of the effluent seem worse. That would be an unrealistic situation, since dilution of the effluent in receiving water would bring the pH very near to the natural level of pH in that water. Therefore we are recommending that toxicity tests for monitoring an effluent be done at a pH that represents the natural pH of the receiving water. Federal regulations and guidelines (EPS 1972) do not specify pH. The Ministry of Environment method (Craig et al. 1983) does not mention a pH for the test, and the Ministry's normal practice is to run lethal tests with pulp mill effluent at whatever pH prevails with the sample.

Low dissolved oxygen increases the apparent toxicity of kraft mill effluent, as would be expected. Very low oxygen cuts the threshold LC50 of bleached kraft mill effluent in half because of the respiratory needs of the salmon being tested. The presence of bleached kraft mill effluent at sublethal levels meant that the fish required higher concentrations of oxygen to avoid respiratory distress (Alderdice and Brett 1957). A similar increase in apparent short-term lethality was documented by Hicks and DeWitt (1971). Whether reduced oxygen also influences the sublethal toxicity of kraft mill effluent has not been studied, but it must be presumed that a similar relationship would exist.

This interaction of low oxygen and toxicity of kraft mill effluent has influenced our considerations of appropriate oxygen concentrations for various levels of protection (see Section 11)

9. ORGANOCHLORINE SUBSTANCES

SUMMARY. (1) A variety of chlorinated organic chemicals are produced by bleaching in kraft mills. The average Ontario bleached kraft mill would produce about 35 tonnes of chlorinatred organic substances per day. About 300 low-molecular-weight organochlorines have been identified in bleach plant waste, but they represent under 10% of the total weight of organochlorines. (2) Chlorinated phenolics and chlorinated resin and fatty acids account for much of the acute lethality of bleach plant effluent. Most of them are lethal to fish at about 1 mg/L or a few mg/L. (3) These low-molecular-weight substances are moderately bioaccumulative in fish, but are readily excreted if the organism moves to clean water. The chemicals are only moderately persistent in the environment, with half-lives estimated as a matter of a week, or a few weeks. Most of them are only partially removed by secondary waste treatment. (High-molecular-weight chlorinated lignins persist for decades but are not very toxic.) (4) The real cause for concern is not these common chlorinated phenolics and resin acids which cause acute lethality and have received the most study. The worry is the unknown degree to which highly toxic and persistent compounds are formed, and escape to the environment. Included among the organochlorines are small amounts of the dangerous chlorinated dioxins, and it can be safely assumed that there are other undiscovered highly toxic substances. (5) Chloroform is a matter of some concern for human health, which suggests that mills should move toward modern bleaching sequences which do not use hypochlorite.

Most people have a general awareness that certain organochlorine substances, particularly the insecticide DDT and the industrial chemicals called PCBs, proved to be dangerous persistent toxicants that accumulated in ecosystems. In particular, predatory animals near the top of food-chains accumulated such man-made persistent toxicants that reproduction was affected, for example in trout in New York state in the 1960s, and in gulls and some other birds along Lake Ontario in the 1970s.

It is not generally recognised that many organochlorine compounds are toxic, including some that have been in common use. For example the substance hexachlorophene was commonly used in soap and patented facial cleansers, not too many years ago. It is still used in hospitals as a cleaning emulsion, at 3% concentration of the organochlorine. And yet a baby powder that contained 6.3% of the substance resulted in poisoning of 204 French children, with 36 deaths (Martin-Boyer et al. 1982).

We are concerned about the release into natural environments of persistent and bioaccumulative toxicants, of which organochlorines are an important fraction. There are recent findings that our industrial society must take much stricter measures to reduce the escape of persistent chemicals. Passino and Smith (1987) report that 476 organic contaminants have been measured in wild lake trout and walleyes from the Great Lakes, compared to only 8 compounds in lake trout from a hatchery. Some of those substances were lethal to an aquatic organism at fractions of a part per million, and organochlorines were well-represented in that more toxic group. Passino and Smith associate their findings with reports on failed reproduction of lake trout from the Great Lakes. Some 50 million small lake trout have been released into Lake Michigan during the last two decades, and a population of mature adults has developed, but with almost no natural reproduction. Both laboratory and field trials indicate that in the industrialised part of Lake Michigan, at least, the failure may be due to accumulation of toxicants, which are passed from the parents to the eggs. Eggs collected from southeastern Lake Michigan were reared in both lake water and clean hatchery water, but in both cases there was almost complete mortality of the newly hatched fish, unexplained except for their burden of persistent toxicants (Willford et al. 1981, Mat et al. 1985).

Our general feeling from such findings is that there should be an immediate start in reducing discharge of persistent toxicants, including organochlorines. As shown in Section 12, there are economic ways to do this in a generic sense (e.g. total organochlorines from pulp mills), and it should be done, rather than delaying for further research to determine just which sub-components are the most toxic.

9.1 General Background

Organochlorines may be regarded as an extremely varied collection of organic molecules, to which one or more chlorine atoms have become attached during the bleaching of pulp. Many such molecules resist degradation in the environment, that is they are persistent. Many of them are toxic, some extremely so, and some of them bioaccumulate in organisms.

About 300 low-molecular-weight chlorinated substances have been identified so far in bleach plant waste, but they represent only a small part, variously described as 3% to 10% of the weight of Total Organically bound Halogens (TOX) contained in the waste (IPK 1982, McKague 1988). About 80% of TOX consists of high-molecular-weight molecules (> 1,000 units, see Fig. 9.1). These have little toxicity but they gradually decompose to low-molecular-weight chlorophenolics which are toxic (SSVL 1985).

The "X" in "TOX" refers to **halogen**, a family of chemical elements known for over a century. Chlorine is by far the predominant halogen in waste waters from bleached kraft mills, so the term "Total Organic Chlorine" (TOCl) is often used. The terminology is further explained in Section 9.

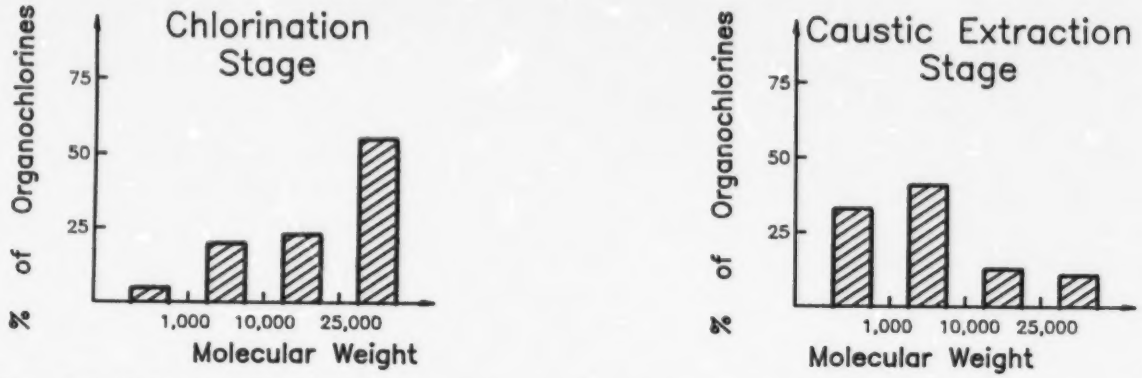

Figure 9.1 Molecular weights of organochlorine compounds discharged from kraft bleached plants.

The "chlorophenols" or chlorophenolics include chlorinated catechols, guaiacols, and phenols. Up to 0.1 kg of these would be formed in conventional bleaching, per tonne of pulp per day. They resist decomposition, and secondary treatment removes only zero to 40 % of chlorophenols from liquid effluent (Oikari and Holmbom 1986). Micro-organisms in the environment may transform them but that is not necessarily the end of the story. Bacterial o-methylation may convert them to chloroveratroles which are not only as lethal to larval fish as the parent chemicals, but also caused deformation of the spine which the parent compounds did not (Allard et al. 1987, Neilson et al. 1984).

Chlorinated thiophenes are another group of substances documented in bleach plant wastes. Thiophenes are similar to a benzene ring with a sulfur atom in the ring. They are lethal to crustaceans at a few mg/L, and some are mutagenic (Carlberg et al. 1987).

The relationship between the amounts of organic chlorine produced and alternative production processes used in various kraft mills is shown in Table 9.1, as estimated by Norström (1987). Other processes which achieve similar reductions in the production of organochlorines are given in a paper by Germgård and Larsson (1983)

Table 9.1 Swedish suggestions for methods of reducing total organochlorines (TOCl) in kraft mill effluent (Norström 1987).

TOCl[1] in effluent kg/ADt	TOX[2] kg/ADt	Mill procedures
≥ 5. kg/tonne	6.5	Conventional chlorine bleach, no biotreatment
3.5	4.5	Oxygen delignification, or special biotreatment.
2.5	3.3	Oxygen delignification plus lagoon.
2.0	2.6	Oxygen delig., ClO_2 and HOCl substitution, lagoon probably required.
0.5	0.7	Probably all the above process changes, with some of extended cooking, NO_2 pretreatment, ultrafiltration, with lagoon treatment. Unproven technology.

The numbers shown in Table 9.1 represent the chlorine attached to organic molecules. The weight of chlorinated organic matter would be 10 times higher (IPK 1982) or 13 times higher (Bengtsson and Renberg 1986). Thus a kraft mill with production of 1,000 tonnes of pulp a day, and conventional chlorine bleaching, would discharge at least 5 x 10 x 1,000 = 50,000 kg = 50 tonnes of chlorinated organic substances every day, or perhaps 65 tonnes or more!

9.2 Toxicity of Organochlorines in Kraft Mill Effluent

With these compounds we are more concerned with their subtle action as persistent toxicants. There is not a great deal of information on that, but we may get some impressions from considering more ordinary toxicity as indicated by LC50s.

Leach and Thakore (1975) evaluated the caustic extraction streams at 6 Canadian kraft mills, and found that the major chlorinated organics in those streams averaged 4.3 times the lethal concentration, assuming that their toxicities added together.

1 TOCL is comparable to, but not identical to TOX.

2 Approximate equivalent TOX added by present authors.

Some overall evaluation is possible from the information summarised by McLeay (1987) on lethality of the more important organochlorines, and their concentration in bleached kraft mill effluent. His information is repeated in part, in Table 9.2, but the ranges of numbers are difficult to evaluate. We have made a rough assessment by assuming that half of a maximum value listed by McLeay might represent an average value. For example on the first line of the table, our assumed concentration of dichlorocatechol in untreated effluent would be 45 ug/L ("parts per billion"). Toxic units, shown in the next column, are calculated on that basis, i.e. TU = (assumed concentration in effluent) / (LC50). When toxic units add up to 1.0 or more, the mixture is predicted to be lethal.

Table 9.2 Ranges of concentrations of organochlorines in bleached kraft mill effluent (ug/L). From McLeay (1987). The calculations to estimate Toxic Units (TU) make some very approximate assumptions (see text).

Organochlorine	96-hr LC50 (ug/L)	Untreated Conc.	BKME TU	Biotreated Conc.	BKME TU
Dichlorocatechol	500-1000	12-90	0.09	1-120	0.12
3,4,5-Trichlorocatechol	1000-1500	120-270	0.14	2-280	0.14
Tetrachlorocatechol	400-1500	22-420	0.28	2-240	0.16
Dichloroguaiacols	2300	22-100	0.02	12-60	0.01
Trichloroguaiacols	700-1000	<10-340	0.24	<1-220	0.16
Tetrachloroguaiacol	200-1700	<10-620	0.36	<1-220	0.13
2,4-dichlorophenol	2800	9-15	0.003	2-51	0.009
2,4,6-trichlorophenol	450-2600	<1-51	0.02	<1-61	0.02
Monochlorodehydroabietic acid	600-900	<10-750	0.625	<1-260	0.22
Dichlorodehydroabietic a.	600-1200	<10-410	0.34	<10-152	0.13
Dichlorostearic acid	2500	<40-552	0.11	<40-268	0.05
		Total	2.2		1.1

The ball-park estimates in Table 9.2 suggest that chlorinated organics should not be ignored as toxicants in whole bleached kraft mill effluent. The toxic units total twice the lethal concentration in our hypothetical untreated effluent, and just over the lethal concentration in biotreated effluent. The tabulation includes practically all of the substances which were listed earlier (Table 8.3) as major toxicants.

A parallel evaluation might be based on the measurements of much the same list of organochlorines, made by Kovacs et al. (1984) for the outlets of aerated lagoons treating the waste at 9 Canadian bleached kraft mills. If the average concentrations are used, along with the LC50s from Table 9.2, these substances in treated bleached kraft mill effluent add up to only 0.2 toxic units instead of 1.1

Thus the organochlorines, by themselves, seem to account for a moderate amount of the acute lethality of untreated or treated bleached kraft mill effluent. There does not appear to be information on the concentrations causing sublethal effects at the whole-organism level but Swedish research shows that they have sublethal toxicity (Section 9.6). Adequate dilution might bring the organochlorines down to thresholds for such overt sublethal effects (again ignoring other categories of toxicants).

9.3 Bioaccumulation and Persistence

The major "traditional" organochlorine toxicants in bleached kraft mill effluent are moderately bioaccumulative. For example 2,4,6-trichlorophenol, trichloroguaiacol, and tetrachloroguaiacol are taken up rapidly by rainbow trout, to concentrations in the liver of a few tens or a few hundreds of ug/g (parts per million, expressed in terms of fat in the liver. This would be about 4 ug/g on the basis of weight of the whole liver.) However, upon return of the trout to clean water, the organochlorines disappear from the liver in a few days (Landner et al. 1977).

Other chlorinated substances accumulate in fish. In a series of papers, Oikari (e.g. 1986) has documented many of them in the bile of fish that live near pulp mills. Total concentrations were more than 1,000 ug/ml (parts per million) for fish that were 1 km from the outfall. Chemicals measured in the bile were 2, 4, 6-trichlorophenol, 2, 3, 4, 6-tetrachlorophenol, 4, 5, 6-trichloroguaiacol, 3,4,5,6-tetrachloroguaiacol, and pentachlorophenol.

Bioconcentration factors appear moderate, being about 400 for 4,5,6-trichloroguaiacol and tetrachloroguaiacol (Renberg et al 1980).

The persistence of organochlorines in the environment varies considerably with the type of compound, and also apparently with the investigator. High-molecular-weight compounds such as chlorolignin gradually decompose to low-molecular-weight organochlorines, but they may be stable for decades in sediments on the bottom of waterbodies (Salkinoja-Salonen et al. 1981). It is the low-molecular-weight organochlorines that pose toxicity problems. From laboratory experiments (Kuivasniemi et al. 1986), it would appear that a half-life of about a week would be appropriate in a natural aquatic situation, for ordinary chlorinated phenols (2,4-di-, 2,6-di-, 2,4,5-tri-, 2,4,6,-tri-, 2,3,4,6-tetra-, and penta-), for the chlorinated catechols (3,4-di-, 3,4,5-tri-, and tetra-), while the half-life would be several weeks for the chlorinated guaiacols (4,5-di,3,4,5-tri-, 4,5,6-tri-, and tetra-). We do not consider these to be "persistent" toxicants.

9.4 Chloroform

SUMMARY. Appreciable amounts of chloroform are formed in some bleached kraft mills, particularly in a hypochlorite bleaching stage. Because it is a presumed carcinogen and is volatile, there has been concern about concentrations in the workplace and near waste treatment lagoons. It does not seem to be a major problem for aquatic organisms.

Very substantially larger amounts of chloroform are produced in a bleach plant if there is a hypochlorite stage, than if hypo is not used, and the amount increases as the charge of hypochlorite increases (NCASI 1987b, Crawford et al. 1987). Concentrations in the whole mill effluent range from 0.5 to 7.0 mg/L (McLeay 1987), but may be 50 or 100 mg/L in bleach plant effluent (NCASI 1987). This can be significant in Ontario mills because of extensive use of hypochlorite.

Since chloroform is volatile, and is probably a carcinogen, there is currently some concern about exposure of people working at mills. Concentrations in the air of the bleach plant could be a problem, although we have not found any published studies of the matter. If there is biological treatment of an effluent with high chloroform, 80% of the chloroform disappears (Beak 1987), most of it presumably escaping to the air. That could be a potential hazard depending on location of the treatment facility and proximity of other human activity. The steps required to reduced organochlorines discharges will modestly result in reductions in the chloroform content of effluent. Refer to discussion of in-plant reduction of chloroform formation in Section 3.7.6.

Chloroform would not appear to be an important hazard for aquatic ecosystems, although it does persist in the water for long enough to trace an effluent plume for several kilometres. However, the toxicity to aquatic organisms is low, and so is the potential for bioaccumulation.

9.5 The Unknown Organochlorines

The preceding sections give the general impression that chlorinated organic substances from the bleach plant of a kraft mill are not extremely dangerous. The toxic, low-molecular-weight ones are not strongly bioaccumulative, nor are they very persistent. Most of the research on those substances is apparently because they have been identified as the cause of the "traditional" toxicity that can be measured by lethality or short-term sublethal effects.

One further thing is, however, most important. Ninety-seven percent of the total amount of organochlorine from a kraft bleach plant has not been identified as specific substances. Certain subtle toxicants such as chlorinated dioxins have recently been identified in some mill effluents. Although they form an infinitesimally small proportion of total organochlorines, and do not contribute significantly to the "traditional" toxicity, they could be creating some real problems (see Section 10). The obvious question is .....

"how many other subtle toxicants in bleach plant waste await discovery?"

We think that question takes precedence over the effects of the more "routine" chlorolignins and chlorophenolics that have been documented by most of the toxicological research to date on kraft mill organochlorines.

The particular organochlorine compounds making up the bulk of the organochlorines in a given effluent are not yet known, will probably never be completely known, and in any case will vary over time. **However, it is assumed that a reduction in total chlorinated organics will proportionally reduce the dangerous ones, and that is the approach recommended here.** Obviously the safest procedure would be total elimination of organochlorines from all discharges. That seems unrealistic at present if we continue to demand high brightness white paper. It is not sufficient to precipitate the organochlorines into the sludge during waste treatment since that merely creates an alternative disposal problem

9.6 Scandinavian Studies

SUMMARY. (1) Swedish industry and government have carried out research programs on environmental aspects of bleached pulp waste for a decade. Much of this was field work in the Baltic Sea, where deleterious effects on biota were documented at distances up to 10 km from a bleached kraft mill, at effluent dilutions of one in a thousand. (2) Some effects seemed to be related to bleach plant waste, since they were found near the bleached kraft mill but not the unbleached one. In that category were erosion of fins of fish and failure or delay of gonad development. (3) Spinal deformities in fish were found near both bleached and unbleached mills, but in the laboratory, the effect was less pronounced for bleaching methods which had reduced use of chlorine. (4) This research provides some evidence that organochlorines formed in bleached kraft mills are dangerous. The current Swedish emphasis on reducing TOCl seems to be derived from a general rationale that many chlorinated organic substances have proven deleterious in past experience.

The Swedes carried out diverse studies under a program "Environmental harmonisation ..." from 1977 to 1981 (IPK 1982), then continued with "Environmental impact of bleach plant effluent" from 1982 to 1985 (SSVL 1985), and "Environment/Cellulose", from 1983 to 1986. Results of the last-named project were largely reported at a conference in Tampere, Finland in June 1987; one of us attended and we have the collected papers from the conference.

The project "Environment/Cellulose" carried out studies in the vicinity of two mills, one unbleached kraft and the other bleached (sequence O(C85+D15)(EO)D on one line and O(C85+D15)(EO)DED on the other).[3] This mill would produce a relatively low level of organochlorines compared to most Ontario mills. Wastes were discharged to the Baltic Sea, which in that vicinity is brackish (0.8% salinity compared to 3.5% for the ocean).

Evidence of such disturbed body chemistry was provided by a whole suite of biochemical/physiological tests on perch (Larsson et al. 1987). Some of the more important observations were enlarged liver, strong induction of mixed function oxidases ("defence enzymes") of the liver, strongly abnormal metabolism of carbohydrates, and drop in white blood cell count. These effects were strong near the mill, but some of them continued to a lesser degree at locations 8 - 10 km away. Dilution of the effluent at those points was estimated as more than 1140 times, i.e. less than 0.1% effluent. The authors make the following statement about similar studies near the unbleached mill: "... a limited investigation on perch caught in the receiving body of water of a pulp mill without bleaching processes showed no or considerably lower effects on most physiological parameters ..." but the details have not yet been published.

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3 "C95 + D5" implies that chlorine dioxide is substituted for 5% of the total chlorine demand in the first bleaching stage. The other symbols are O for oxygen, E for extraction, and H for hypochlorite, as further explained in Section 3.3.2.

Fish with deformed spinal columns were found near Baltic pulp mills by Bengtsson (1987). Exposures in the laboratory had allowed him to associate the effect with changes in chemical and mechanical properties of the bone (e.g. strength and resistance to rupture). Perch showed these symptoms whether they were collected 1 km from the bleached mill or 0.5 km from the unbleached one. Further lab exposures allowed Bengtsson to conclude that bone damage from effluent of bleaching pulp with chlorine dioxide (DEDED) was no worse than that from unbleached operations. Treatment by aerated lagoon resulted in no bone damage at a mill using oxygen delignification and high chlorine bleaching of pine (O(C84/D16)EDED). Without the lagoon, there was bone damage from a lower proportion of chlorine (O(C52/D48)EDED).

Perch accumulated organochlorines from the bleached kraft mill studied in "Environment/Cellulose". Near the mill, extractable organic chlorine (EOCl) was 200-400 mg/kg (fat weight), and gradually declined to a background level of 50-120 mg/kg at 11 km from the mill. Near the unbleached mill, EOCl was only 12-70 mg/kg (Södergren et al. 1987). High concentrations of EOCl were also found in nearby sediments. The chlorinated chemicals 1 km from a mill were mostly the ones common in effluents. At distant locations (18 km) there was still appreciable EOCl, but the substances present did not at all match those of bleached kraft mill effluent; either they were from other sources or had been transformed (de Sousa et al. 1987).

Artificial ecosystems simulated the community along the shores of the Baltic. These were large tanks (7.5 m^3) with gradual replacement of testwater, and a semi-natural community of sea-weed, invertebrates, and fish. Adding bleached kraft mill effluent at 1% caused tissue damage to the gills and livers of flounders in the systems, and increased the numbers of parasites on the gills (Lehtinen et al. 1984).

Such studies with artificial ecosystems are also reported by SSVL (1985). The experiments on sublethal toxicity used six different kinds of kraft effluent at very weak concentrations. Results have apparently not been published in scientific journals, but the summaries in the general report give some information that appears dependable. All six mill effluents caused meaningful sublethal effects on fish growth and populations of invertebrates at the low concentration of 0.25% (1 in 400 dilution). The effects were severe for the effluent from conventional bleaching and slight for those with oxygen delignification and higher chlorine dioxide substitution. In tests at 0.05% effluent (1 in 2000 dilution) the conventionally-bleached effluent caused meaningful damage, but the other effluents did not. The six effluents were rated for "severity of environmental damage", as summarised below, with the most damaging kind of bleaching at the top and the best at the bottom. Effluents with the same number (3) were approximately equal in environmental effect.

1. (C95 + D5) EHDED	
2. (C87 + D13) EDED	plus aerated lagoon
3. O (C83 + D17) EDED	
3. O (C85 + D15) EDED	partial treatment in aerated lagoon
3. O (C52 + D48) EDED	
4. O (C84 + D16) EDED	plus pilot aerated lagoon

The Swedish studies in the Baltic and in artificial ecosystems indicate measurable effects at 1/400 dilution (0.25% effluent, or about 0.01 of the LC50). The studies also show some evidence of meaningful effects at dilutions of 1/1000 to 1/2000, i.e. in 0.1% effluent (0.004 LC50) or less. Those concentrations are extremely low, much lower than no-effect concentrations in laboratory experiments (Section 8.2) and in North American ecosystem experiments (Section 8.6).

It may be that other toxicants in the Baltic Sea are acting in concert with those from pulp mills, and lowering the apparent effect-concentrations. Certainly the Baltic has many sources of pollution, and signs of probable severe problems with persistent toxicants. For example some of the Baltic grey seals have deformities of the flipper skeleton, loss of teeth, destruction of kidney cortex, and show failure in reproduction (Vaste 1986). The problems in the seals are accompanied by elevated body residues for a number of contaminants such as PCBs and pesticides.

Recent field studies around Ontario mills have not reported findings like these Swedish ones, for example we have not seen documentation of fin erosion. Perhaps this is because the Ontario surveys have not looked for such effects, at least not with the thoroughness of the Swedish studies. Alternatively, perhaps northern Ontario's receiving waters can assimilate more pulp mill effluent because they are relatively free of other pollutants. It would be desirable to conduct methodical studies around Ontario mill-sites, for example checking fish populations for fin erosion, malformations, and tumours.

It is partly on the basis of evidence like that reviewed above, that Sweden is moving so strongly to reduce the use of chlorine in bleach plants. Clearly there is evidence that the toxicological problems associated with bleached kraft mill effluent are more severe or qualitatively different, than those associated with unbleached mills. The evidence reviewed above is not strong, but no doubt it will become stronger. The Swedes appear to be operating in large part, on a general principle that several chlorinated organic chemicals have been environmental disasters in the past, and that therefore there should be a general emphasis on reducing organochlorines, more than the other components of pulp mill waste.

We think that the Swedes are probably correct, and offer the following thoughts.

> Looking back over a few decades, some of the worst bioaccumulative toxic substances have been chlorinated organics such as DDT and PCB. They accumulated in food chains, and there was loss of reproductive capacity in birds and some other animals. Those and some other persistent toxicants had spread themselves everywhere in ecosystems before scientists were aware of any problem.
>
> A single big bleached kraft mill may put out 50 or more tonnes of chlorinated organic substances every day, containing hundreds or thousands of unidentified substances.
>
> The recent furor over dioxins confirms that there are indeed small amounts of notable substances in the wastes from at least some kraft mills, and there does not seem any reason to wait for the discovery of other subtle toxicants.
>
> There are alternative processes for bleaching which do not produce so much organochlorine. Some of them are economically advantageous, while others may at least not have an economic penalty. It seems evident to us that Ontario mills should start now, to initiate a strategy for long-term reduction in output of organochlorines.

9.7 Organochlorines in the Product

SUMMARY Organochlorines in pulp have recently become a serious concern, partly because some major buyers of kraft pulp in the European Common Market have indicated that they are considering regulating the organochlorine content of imports to levels which could prevent Canadian mills selling into their markets, and partly because the organochlorines are distributed in the environment when these pulps are converted to paper and eventually discharged. Some US customers have recently requested information on dioxin content of Ontario market kraft pulp.

Concern has arisen about organically bound chlorine in pulp and paper products. The attention of the media has been focussed on the chlorinated dioxins, which are a sub-set of the vast range of organochlorine substances, and are discussed in some detail in Section 10 of this report.

We are aware of several market kraft mills in Canada and Sweden who have been requested by German customers to certify the organochlorine content of their pulp being shipped to Germany, and understand that similar requests have originated in Switzerland. German authorities have indicated their intention to regulate organochlorines to 1 kg/t in imported pulps, and 0.1 or perhaps 0.01 kg/t in paper sold in the country. While those levels are merely tentative, and cannot be fully evaluated until the details of the analytical protocols are defined, they raise concerns about the future marketability of Canadian pulps in Europe. They also suggest that if a technologically advanced country like Germany is concerned, then other countries should at least investigate the environmental significance of organochlorines in paper under their own conditions.

There are very few data available on the organochlorine content of Canadian kraft pulps. Industry sources who prefer not to be identified have indicated values in the order of 0.02 - 0.2 kg/t pulp. In view of the recent interest expressed by their customers, we expect that many mills will develop data on the organochlorine content of their pulps during 1988.

There are essentially two ways of reducing organochlorines in the pulp, both of which involve modifications of the bleaching conditions. The mill operator can either reduce generation of these compounds, or ensure that the organochlorines produced are discharged of the sewers and the atmosphere, instead of remaining with the pulp. We are not aware of any techniques for diverting organochlorines from the pulp to the effluents or atmospheric emissions, but the incentive to develop them has only recently arisen. Considerations for regulating organochlorines in effluents must take account of these aspects.

Organochlorine content of bleached kraft effluents is typically 3 -11 kg/t pulp, so that in the order of 2% of total organochlorine compounds formed in the bleach plant seem to remain with the pulp. This indicates that there is little risk of organochlorine content of the effluents being increased significantly because of customer pressures to eliminate it from the pulp. However, data on the organochlorine content of pulps is very sketchy and unpublished, since there was no interest in it until recently, and there are, as yet, no accepted testing protocols.

Trace amounts of dioxins have been found in kraft pulps during a five mill survey in the US, with values up to 51 ppt, mean 13.9 ppt (Amendola 1987). Unpublished data we have from several mills are in this range, and several correspondents within the industry and government organisations have confirmed that their organisations have found dioxins in most of the bleached kraft pulps that they have had analysed. Extensive testing of pulps from many mills is under way at the time of writing, so we can expect to see

more data before mid 1988. Longer term programs in Canada and the US will probably result in pulp and wastewaters from all North American mills being tested for dioxins and furans in the near future Some mills report having been questioned by US customers on the dioxin content of their products, including market kraft.

Technologies for reducing the generation of organochlorines are discussed in Section 3 with respect to reducing organochlorines in the mill effluent.

9.8 Calculation of Organochlorine Content of Effluents

Germgård (1983) proposed the following equation for calculation of the organically bound chlorine (TOCl) [4] discharge from kraft bleach plants, and it has become quite widely accepted.

$$\textbf{Organic chlorine} = k \times (C + H/2 + D/5) \text{ kg/tonne pulp}$$

where k is a constant in the range 0.07 to 0.11 if C,H, and D are in the units kg/t pulp and the Organic chlorines are expressed according to the TOCl analysis procedure (Sjostrom 1982)
C is total elemental chlorine charge
H is the hypochlorite charge, as equivalent chlorine (= 1.05 x NaOCl)
D is chlorine dioxide charge as equivalent chlorine (= 2.63 x ClO_2)

The above equation has been quite widely used in Scandinavian literature, and many statements which one might presume to be based on analysis of mill or laboratory data are actually based on the equation, although authors rarely mention the value they selected for the k factor. Earlier literature proposed values from 0.05 to 0.07 for k, but personal communication (1987) with Germgård and analysis of various reported data for TOCl discharges suggests that a value of 0.09 is the most appropriate, and all calculations of TOCl discharges in this report are based on this value. Where APHA TOX data are to be calculated, as recommended for future regulations in Ontario, a multiplier of 1.3 must be used, effectively raising the **value of "k" above to 0.12.** Refer also to Section 9.9 concerning conversion from TOCl data to APHA TOX.

In view of the approach we have discussed in Section 9.10 below for determination of the quantities of organochlorines discharged from mills for regulatory purposes, the **exact value selected for k is relatively unimportant**.

The foregoing equation ignores any treatment of the bleach plant or whole mill effluents, so we have assumed that biological treatment of whole mill effluents can remove 35% of the TOX, as discussed in section 5.3.1.

It is essential to be able to predict the effect of modifications in the bleaching sequences and chemicals used, in order to develop sound Control Orders, and to engineer improvements in bleach plants. We therefore recommend that mills be allowed to elect to determine organochlorine emissions by calculation from the above-mentioned equation until better techniques become available, as is sure to happen within a few years, given the active level of research. We recognise that data will probably become available which will demonstrate some inaccuracy in the above equation, but consider that using the equation is the

4 In this Section, note that "TOCl" refers specifically to the values obtained by analysis using intrafiltration and XAD resin according to Sjostrom et al (1982)

only realistic way of achieving any progress in reduction of the organochlorine emissions in the near future. To express the point another way, it is unreasonable to expect an industrial plant to agree to invest substantial sums to comply with a limit on TOX unless the engineering knowledge exists to design and build

9.9 Analytical Determination of Total Organochlorines

There are several potential methods for determining the organochlorine content of wastewaters, and we have categorised those we consider the most useful as follows:

DIN 38409 German norm
TOCl Swedish common practice (Sjostrom et al 1981)
APHA 506 US Standard Method (APHA et al. 1985)
AOX Swedish method under development (Bethge 1987)

9.9.1 Swedish TOCl Analysis

Most of the Scandinavian literature on organochlorines is based on analyses "Total Organically bound chlorine" by the "TOCl" method described by Sjostrom (1981). Briefly, the procedure involves extraction of the organochlorines from the effluent sample by both XAD resin (for lower molecular weight material) and ultrafiltration, although one or other of those processes is omitted when it is considered unimportant. The chlorine content of each recovered fraction is determined by Shoniger combustion as described by Eriksson (1976). Before analysis the sample is aged for a week to stabilize the TOCl content. This causes the more volatile organochlorines, such as chloroform, to escape. Samples may be frozen for storage prior to analysis if desired, but one week aging at 4 deg C is still required. The laboratory work requires 1-2 days, and the procedure does not lend itself to automation. The considerable labour involved and the delay of one week in obtaining the analytical results is very inconvenient when performing any process studies or when attempting to control effluent quality.

9.9.2 German AOX (DIN) Procedure

German researchers appear to prefer the technique described by the German Society of Chemists **(DIN 38409)**. This is often described as **("AOX")**, but the term can be confusing since the Swedish Pulp and Paper Research Institute (STFI) is in the process of developing a similar procedure that they also describe by the name AOX. The German procedure involves absorbing the organic matter from the effluent sample on activated carbon, and then burning the carbon to determine the halogen content coulometrically. There is no specification for sample pretreatment in the AOX procedure, and one would have to be developed before AOX could be recommended as a basis for regulatory action. AOX analysis is more convenient than the previously mentioned TOCl procedure, and about 10 can be performed in one day. Commercial apparatus is available in Canada at a cost of approximately $30,000. The apparatus is moderately delicate and requires suitable installation in a halogen free environment, so the actual cost of equipping a laboratory and training staff would be in the order of 3 times the basic equipment cost

9.9.3 Swedish AOX Procedure

Bethge (1987) concluded that the AOX procedure is preferable to the above mentioned TOCl and reports that the Swedish pulp industry is in the process of evaluating the techniques and intends to develop a **Swedish AOX analytical protocol** by the end of 1988. This investigation is considering several methods of absorbing the organics on carbon, including passing them through a tube containing the carbon, or mixing the effluent sample with carbon in a flask, but at the time of writing, the latter seems to be preferred. Bethge has advised that the Swedish procedure will be finalised by late 1988.

9.9.4 APHA Method 506 Determination of Organic Halogen

Standard Methods (APHA et al. 1985) describes a method for determination of Total Organic Halogen, which it calls "TOX". To reduce confusion at critical points in this report, we have referred to total organic halogen determined by this method as "APHA TOX" The latter is considered as consisting of Purgable Organic Halogen ("POX") and Non-Purgable Organic Halogen ("NPOX").

This procedure refers to total organic halogens, rather than total organic chlorine, but the difference is insignificant in the bleached kraft mill wastes since chlorine is by far the predominant halogen.

The procedure is similar in principle to the German and tentative Swedish procedures described above, but was developed for a wide spectrum of applications from industrial wastes to drinking water, whereas Swedish methods are developed specifically for pulp industry wastes.

Briefly, the organic material from the sample is concentrated on granular activated carbon, inorganic halides are displaced by nitrate ions, the carbon is pyrolised and the product gas, including the hydrogen halides formed, is passed though a microcoulometric titration cell where the amount of halide present is determined.

Extensive testing by Lafleur and Dodo (1988) has shown that the procedure is suitable for pulp mill wastewaters, with precision within 4%. They concluded that interference by non-organic chloride was not a significant analytical problem, except perhaps in the analysis of receiving waters.

This method assumes fresh samples and includes the volatile organochlorines, whereas Sjoström (1982) estimated that about 6% of the organochlorine was lost during the mandatory one week stabilization in the TOCl procedure for chlorination stage effluent. It is logical to assume that the organochlorine loss in stabilising a biologically treated effluent would be insignificant.

This procedure is the most commonly used in Canadian and US research projects, including the extensive work by Bryant et al. (1987) on organochlorine removal in aerated lagoons.

9.9.5 Which Analytical Method?

Methods for measuring total organic chlorine/halides are obviously in a state of flux. In selecting a suitable organochlorine analysis procedure for Ontario, we consider it essential that the method eventually adopted be in use in one or more of the leading countries in the field, so that Ontario can benefit from research outside the province, and also contribute to it effectively.

We have examined the available information referred to above, and discussed the current experience with many workers in the field, and conclude that the most reliable and suitable protocol is APHA TOX Method 506. It is very similar to the German and projected Swedish approaches., and has been extensively verified as suitable for kraft mill effluent testing by NCASI (Lafleur and Dodo 1988)

We are advised that the Ministry's laboratories are investigating an analytical method "based on the Swedish AOX", and are concerned that this may lead to a different analytical technique being used in Ontario than in the US. In view of the extensive work already performed on the development of the APHA procedure, we question the need to develop further analytical technology, whether by Ontario or Bethge's group at STFI in Sweden. It may be necessary to further specify sample collection and handling.

We believe that most of the (unpublished) organochlorine analyses of Canadian kraft mill effluents performed to date have used a procedure very similar to the German DIN 38409, so caution must be used in comparing them with results of APHA TOX analyses. We have been unable to find any published data comparing the results of these two methods, but would expect TOX to be around 10% higher than DIN 38409 for most effluents, and little different for biologically treated effluents.

Sjostrom's TOCl procedure would have the significant advantage that extensive engineering and environmental studies in Sweden have used it, which would facilitate technology transfer in the short term. However, the procedure is about to become obsolete(Bethge 1988), and has some practical weaknesses, so we do not consider that it would be desirable to adopt it in Ontario.

Bethge (1988) estimated that for traditional bleaching processes, the AOX procedure would give results about 10%-30% higher than the Swedish TOCl procedure. Discussions with him and other experienced analytical chemists have led us to **recommend that, for the purposes of this report, a conversion factor of 1.3 be used to convert Swedish TOCl data to values which would be determined by the APHA 506 TOX procedure.**

9.10 Determination of TOX Content of Effluent

It is clear from the foregoing that the Ministry and the industry must have a suitable means of determining the organochlorine content of effluents if discharges to the environment are to be reduced. While we recommend the APHA analytical procedure for determination of TOX, it has the serious short term disadvantage that few of the data available on organochlorine discharges from various bleaching processes are based on it.

If Germgård's equation described in Section 9.7 is used to determine organochlorine discharges, it would reduce the uncertainties mills must face in engineering modifications to the bleach plants to reduce organochlorine discharges, thus facilitating implementation of a practical program.

We therefore recommend that, pulp producers have the option of using either the APHA TOX analytical procedure, OR the Germgård equation described in Section 9.8 above for determination of organochlorine discharges from the mill, prior to biological treatment. Reduction in organochlorine concentrations across effluent treatment systems should be determined by analysis. This recommendation is made in the knowledge that the values calculated will not agree exactly with those determined by analysis.

We further recommend that the situation be re-evaluated when sufficient operating experience is available with bleach plants modified to reduce organochlorine discharges, and using APHA TOX analysis of effluents. We expect that this information will be available in 4 to 5 years, at which time the equation can be abandoned for regulatory purposes, and the conventional approach of using the results of analyses carried out according to a standard protocol.

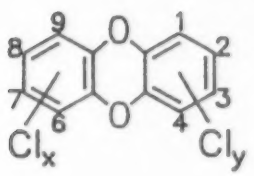
We consider that the calculation technique is much more practical, at present, and allows for early starts on control which is highly desirable. The calculation is based on the assumption that mills will continue to bleach with currently known processes, which is realistic in the short to medium term, but unrealistic in the long term. Germgård's equation does not take account of external effluent treatment processes, nor would it give credit to any process to recover and destroy organochlorines by "physico-chemical" treatment. It is therefore essential to allow pulp producers a choice of chemical analysis of APHA TOX as the basis of regulating their organochlorine discharges.

10. CHLORINATED DIOXINS and FURANS

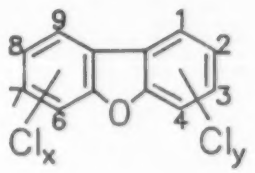
"Concern that this material is harmful to health or the environment may be misplaced. Although it is toxic to certain animals, evidence is lacking that it has any serious long-term effect on human beings."
Header of an article "Dioxin" in the February 1986 issue of Scientific American, by F.H. Tschirley.

The news media provided considerable coverage of "dioxin" in paper products in the autumn of 1987, and the concern was for cancer in people. However, the most toxic chlorinated dioxin is extremely variable in its effects on different mammals, and there is no scientific documentation that it has caused cancer in humans. Chlorinated dioxins and furans in paper products pose a very small risk, but they signal a serious question about total organochlorines in kraft mill waste.

We have made use of some previous reviews, particularly a thick and excellent criteria document of the Ministry of the Environment, with superb coverage of previous information on these contaminants (MOE 1985). Pulp mills and paper products received no attention in the Ministry document, since that concern arose after its 1985 publication. We also used a thorough review sponsored by the US paper industry (NCASI 1987a). Unreferenced data in our report should be credited to the above pair of reviews, although crucial papers for our recommendations were obtained in the original. Other useful orientation came from reviews by Tschirley (1986) and Poland and Knutson (1982). The two major reviews (MOE 1985, NCASI 1987a) arrived at the same estimate of acceptable daily intake of chlorinated dioxins by humans. We agree with that estimate.



chlorinated
dibenzo–p–dioxins



chlorinated
dibenzofurans

Fig. 10.1 Diagrams of chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans. The diagrams indicate the presence of an indefinite number of chlorine atoms. For example, 2,3,7,8 tetrachloro-p-dioxin would have four chlorines attached at those positions as numbered in the diagram.

10.1 The Nature and Sources of Chlorinated Dioxins and Furans

SUMMARY. (1) The "dioxin" of the news media can be translated as two families of chemicals, the chlorinated dibenzo-p-dioxins and the chlorinated dibenzofurans. Those families include 210 substances, two of them particularly important from a toxicological viewpoint. They are 2,3,7,8-tetrachloro-p-dibenzodioxin (2378-TCDD, a molecule of two benzene rings joined by atoms of oxygen, with 4 added chlorines), and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF, similar but with only one oxygen to join the benzene rings). (2) The main sources of 2378-TCDD and 2378-TCDF are various unintended by-products of human manufacturing, or burning of wastes. Those particular chemicals are prominent in kraft mill wastes and so those wastes are of some concern in the total environmental flux. Other sources tend to generate less toxic members of the chemical families, such as molecules with seven or eight chlorines. Increased amounts of these contaminants have been in the environment for 3 or 4 decades but are better documented in the last few years because of improved analytical procedures. (3) Chlorinated dioxins and furans are almost insoluble in water, so they tend to travel through ecosystems on particles or as residues in living organisms. (4) Potential toxicity of these chemicals is measured in "parts per trillion", more scientifically expressed as nanograms per litre or nanograms per kilogram.

Two groups of compounds should be considered together, the polychlorinated dibenzo-p-dioxins and the polychlorinated dibenzofurans. In our report we will use the abbreviations shown below in quotation marks because we wish to distinguish between the chlorinated molecules and the ordinary dioxins which exist as unchlorinated molecules.

Polychlorinated dibenzo-p-dioxins	"PCDDs" or "chlorinated dioxins"
Polychlorinated dibenzofurans	"PCDFs" or "chlorinated furans"
Included within those general groups are the	
Tetrachlorodibenzo-p-dioxins	"TCDDs"
Tetrachlorodibenzofurans	"TCDFs"
And within those subgroups, the specific chemicals of most interest are	
2,3,7,8-tetrachlorodibenzo-p-dioxin	"2378-TCDD"
2,3,7,8-tetrachlorodibenzofuran	"2378-TCDF"

We are focussing on those last two specific chemicals, since they are the only ones of appreciable toxicological interest in bleached kraft mill wastes (Amendola et al. 1987). Also, as residues in fish from the Great Lakes and from locations downstream of pulp mills, the major chlorinated dioxin is 2378-TCDD and the primary chlorinated furans are 2378-TCDF and 2,3,4,7,8-pentachlorodibenzofuran (Stalling et al. 1983). The isomer 2378-TCDD is acknowledged to be the most toxic of any of these chemicals, and this is the one generally meant in references to "dioxin" in the press. If other sources of human exposure are considered (air pollution, food other than fish, soil contamination) the most-toxic 2378-TCDD is "a very small percentage of the PCDD and PCDF isomers" (MOE 1985). Therefore the discharges of 2378-TCDD from pulp mills and subsequent accumulation in fish gain appreciable importance as a potential source of danger to aquatic ecosystems and to human consumers.

There are 75 different PCDDs and 135 different PCDFs, all with the general structures indicated in Fig.10.1. The various chemicals differ in number of chlorine atoms attached to the basic molecules, and in the positions of those chlorines. Those molecules with four chlorines are the most toxic, and toxicity decreases as more chlorines are added, through the series with 5 chlorines (penta), 6 (hexa), and the

relatively non-toxic 7 (hepta) and 8 (octa) forms. The chlorinated furans show a similar pattern of toxicity but overall they are less toxic compared to chlorinated dioxins (see below for ratings).

These chemicals are almost insoluble in water, and so they tend to travel on particles or accumulate in sediments and organisms. The solubility of 2378-TCDD in water has been estimated recently as 20 nanograms per litre ("parts per trillion") (Adams and Blaine 1986, NCASI 1987a). It should be strongly bioaccumulative in animals, because of its high solubility in octanol (i.e. very fat-soluble), and a remarkably high value of 6.6 for the logarithm of the octanol-water partition coefficient. Thus it tends to be easily stored in the fats of animals, but by the same token is not found in plant tissues to any extent, because of the low fat content of most plants. Presumably because of this lack of accumulation, "plants are relatively insensitive compared with animals" (MOE 1985).

In this section of the report we have used "parts per trillion" (ppt) as the units for concentration,although precise scientific terminology would use either nanograms per kilogram or nanograms per litre. We hope that the reader appreciates this astonishingly low proportion, and provide the following illustration. Take the floor plan of a typical house and build it as high as the CN Tower. Fill it with water. Now add one drop of ink .... mix thoroughly .... and the solution will be at a concentration of one part per trillion. We are impressed that chemists can measure 2378-TCDD at such concentrations. One nanogram (ng) can perhaps be visualised by starting with an A.S.A. (aspirin) tablet, which will weigh about 400 milligrams (mg). Carefully divide the tablet into 400 equal parts. Take one of those parts and divide it into 1,000 equal particles; each of those is one microgram (ug). Now chop up one of those particles into 1,000 equal pieces and they will each be one nanogram!

Chlorinated dioxins and furans are not industrial chemicals, but by-products created accidentally in manufacturing other chemicals, particularly trichlorophenol and the herbicide 2,4,5-T (2.4.5-trichlorophenoxy acetic acid). Presence of the contaminants has been discovered through many incidents in chemical manufacturing when workers suffered from chloracne, a skin disease caused by several chlorinated organic chemicals, and appearing similar to the acne that is prevalent in teenagers. A variety of chlorinated dioxins and furans are found as contaminants in useful chlorinated phenols, such as pentachlorophenol.

Chlorinated dioxins are also apparently created by combustion, particularly incineration of municipal garbage and burning of wood that has been treated with chlorophenol preservatives. Burning of leaded gasoline in automobiles is a source, although that is not so for unleaded and diesel fuels. Evidence from lake sediments indicates that "natural" combustion such as forest fires is not a large source of chlorinated dioxins. Lake sediments laid down before 1940 contain about 10 ppt from largely natural sources (Czuczwa et al. 1984). Residues in fish also show that aerial fallout in non-industrialised areas, such as might occur from forest fires, is not a big source of contamination. Fish from an isolated lake on Isle Royale in Lake Superior had no detectable chlorinated dioxins, and had lower concentrations of PCDFs (15 ppt total) than did fish from anywhere else in the Great Lakes (Stalling et al. 1983, 1985). Although Sheffield (1985) estimated that forest fires together with burning of wood wastes constituted the most important source of PCDDs in Canada, that has been questioned as an over-estimate (NCASI 1987a). Sheppard has pointed out (personal communication) that his 1985 estimate was very preliminary, and was extrapolated from wood burning in a stove.

The importance of pulp mills as a source of PCDDs and PCDFs, relative to other sources, has not yet been quantified exactly. We make some comparisons in Section 10.8 and conclude that wastes from bleach plants of kraft mills can be of some importance.

10.2 TEQs or Toxicity Equivalent

SUMMARY. The most toxic of all the chlorinated dioxins and furans is 2378-TCDD. Other isomers may be expressed as approximate "Toxicity EQuivalents" or TEQs of that substance, by applying appropriate factors.

The 210 PCDDs and PCDFs differ greatly in toxicity. For example those with 8 chlorines (the octachlorinated dioxins and furans) are often more abundant than other forms, but have practically no toxicity. Accordingly systems have been set up to express concentrations of these substances in terms of their equivalent in toxicity of the most toxic one, 2378-TCDD. The systems are very approximate and incorporate many assumptions, but nevertheless allow us to approach a rational assessment of hazard from a mixture. An Ontario document contains a recommended set of equivalents (MOE 1985). We repeat them in the Table 10.1, and suggest some revisions. We have used the changed factors in this report.

To use the values in Table 10.1, the weight (or concentration) of a given compound is multiplied by its TEQ, the factor listed beside it. The result is the approximate equivalent of 2378-TCDD. After calculating equivalents for each of the components of a mixture, they are added up to yield the total Toxicity EQuivalent or TEQ of 2378-TCDD. Except for the first three items in Table 10.1, the only substances included in the tabulation are ones that are chlorinated in at least three of the four positions 2, 3, 7, and 8; "other" refers to such substances.

Table 10.1 Toxicity EQuivalents for isomers of chlorinated dibenzodioxins and dibenzofurans.

MCDDs	(Monochlorinated)	0.0001	
DCDDs	(Dichlorinated)	0.001	
TrCDD	(Trichlorinated)	0.01	
2378-TCDD	(the standard)	1.0	
other TCDDs		0.01	
2378-TCDF		0.5	[we recommend 0.1]
Other TCDFs		0.5	[we recommend 0.01]
PeCDDs	(2378 and other)	0.1	
PeCDF with 2378 + 1	(Pentachlorinated)	0.5	[we recommend 0.1]
Other PeCDFs		0.5	[we recommend 0.01]
HxCDDs & HxCDFs	(Hexachlorinated)	0.1	[we recommend 0.05]
HpCDDs & HpCDFs	(Heptachlorinated)	0.01	[we recommend 0.005]
OCDDs & OCDFs	(Octachlorinated)	0.0001	[we recommend 0.00001]

We recommend the changes in TEQs indicated in Table 10.1 because the rationale in the document (MOE 1985) appears overly conservative. We have used geometric averages on the relative toxicity data shown in the Ministry's report, to arrive at factors for those isomers chlorinated on positions 2,3,7, and 8, (most of the scientific research is on those isomers). We have used other data in the report, or further factors of

one-tenth, for "other" isomers of a category. Those changes produced our recommended factors which are somewhat closer to recommendations from other places, and closer to more recent estimates by US EPA (NCASI 1987a and G. Amendola, US EPA, Westlake, Ohio, personal communication). In particular, the recommendations for 2378-TCDF and 2378-PeCDF are thought to be more realistic. The recommended lowering to 0.01 for other TCDFs and PeCDFs is a compromise, since EPA suggests 0.001 and other sources suggest zero in most cases. Similarly the values recommended in the last three lines, for Hexa, Hepta, and Octa compounds, are more realistic on the basis of data cited by MOE (1985); many other agencies suggest lower values or zero for HpCDDs and HpCDFs, and zero for OCDDs and OCDFs.

10.3 PCDDs and PCDFs in Relation to Fish and Other Aquatic Organisms

SUMMARY. In Canada, 20 ppt of 2378-TCDD in fish is considered a limit for consumption by humans. Larger fish from some polluted locations may contain that much or more. Whether or not the residues affect the fish has not been documented, but the chlorinated compounds accumulate at higher levels in the food web such as fish-eating birds.

Waterborne 2378-TCDD and 2378-TCDF are incredibly toxic to fish, respectively 10,000 times and 1,000 times as toxic as the insecticides endrin and toxaphene, previously considered the most toxic chlorinated hydrocarbons (Mehrle et al. 1988). The 56-d LC50 of 2378-TCDD for rainbow trout was 0.046 ppt, and the lowest concentration tested, 0.038 ppt, affected growth. The chlorinated furan was an order of magnitude less toxic. Some earlier toxicity tests had procedural problems and yielded less dependable estimates of toxicity.

The same experiment by Mehrle et al. (1988) indicates that the dioxin and furan residues recently found in wild fish may not, by themselves, be directly harmful to the fish. Most surveys of North American fish show concentrations of 10 ppt or less, with values ranging up to 60 ppt in some Lake Ontario fish (see below). Those concentrations are lower than the body level of 930 ppt found in the laboratory experiment, among fish suffering effects on growth (caused by 0.038 ppt in the water).

Another experiment estimated that 2.3 ppt of 2378-TCDD in the food of rainbow trout for 3.5 months produced slight liver damage but no other apparent effects (MOE 1985). We have not found ecosystem modeling to put that finding into perspective, but bioaccumulation in predatory animals that eat fish must be of primary concern (see end of this section). Similarly, residues of PCDDs and PCDFs can be of major interest for human consumers of fish, and that is reviewed immediately below.

Canada Health and Welfare has established a guideline of 20 ppt of TCCD for consumption of fish, and the Ontario Ministry of the Environment has the same limit as a "Consumption Guideline" for sport fish (i.e. 20 parts of the dioxin in a trillion parts of the fish, wet weight, to be eaten by humans). The US Food and Drug Administration (FDA) considers fish to be about the only human food that accumulates appreciable amounts of 2378-TCDD. FDA advises that edible portions of fish with up to 25 ppt of 2378-TCDD can be eaten without an unacceptable risk, fish with 25 - 50 ppt should not be eaten more than twice a month, and fish with more than 50 ppt should not be eaten at all. The US EPA considers that for lifetime consumption of fish, there should not be more than 0.069 ppt of 2378-TCDD, an unrealistically low level that is explained below.)

For farm animals, there are relatively few measurements of residues but MOE (1985) summarises some of them. Picking worst-case situations, and expressing approximately as toxicity equivalents (TEQ) of 2378-

TCDD, poultry fat might contain up to 5 ppt TEQ, pork 0.4 ppt, beef to 0.05, and eggs up to 0.001 ppt TEQ. Most of the isomers found were the highly chlorinated, less toxic ones.

Compared to those domestic food items, concentrations in fish can be much higher, and furthermore the fish may contain appreciable proportions of 2,3,7,8 isomers. For example, extremely high levels of 18 - 810 ng 2378-TCDD/kg were found in Vietnamese fish from areas sprayed with herbicide, according to NCASI (1987).

In Ontario, MOE (1985) finds that most fish from the upper Great Lakes including Lake Erie have little 2378-TCDD, being below detection limits of 10 or 1 ppt. Even from the lower Niagara River, polluted by US chemical dumps, and from Lake Ontario, many fish were below detection limits for this chlorinated dioxin, and most were below 10 ppt. Larger fish such as lake trout were higher, with average content from 8 to 27 ppt. General agreement with those concentrations was shown among the fish sampled by Stalling et al.(1983, 1985). Whole fish from the Great Lakes were low in 2378-TCDD residues for the most part, but those sampled from industrialised Saginaw Bay had 26 - 85 ppt, and Lake Ontario samples were elevated in general (26 - 60). A composite sample of three carp from the Niagara River, where these champion fish had been in close proximity to leakage from the US waste dumps, had 417 ng 2378-TCDD/kg plus 327 of other PCDDs plus 1020 of PCDFs.

A large survey of fish in various parts of the USA was carried out by EPA (1986). All fish and shellfish from marine waters (i.e. salt water) had very low or non-detectable levels of 2378-TCDD. Of 394 freshwater sites sampled, the fish at 282 sites had non-detectable concentrations of 2378-TCDD, and at the remaining 112 sites, two thirds of the levels were less than 5 ppt (NCASI 1987).

In the EPA survey, fish from some rivers that received kraft mill wastes (Androscoggin R., Maine, and Rainy R. at International Falls, Minnesota) had concentrations of 20 - 85 ppt in the whole body, but concentrations in the edible fillets averaged about 30% of whole-body levels. Carp in a reservoir downstream from several mills in Wisconsin had concentrations from 9 to 47 ng 2378-TCDD/kg in the whole body, and 3 - 23 in the fillets. A commercial fishery was closed down. Concentrations were also high in fish from the Flint R. (Michigan) which does not receive pulp mill effluent. An Ontario study reported that 2378-TCDD was below detection limits in 26 of 42 fish collected in Rainy River below a bleached kraft mill. The remaining 16 fish had only 1 to 9 ppt, considerably lower than EPA results for the same river (MOE, press release, July 17, 1986). Twenty fish from the inner harbour at Thunder Bay and the mouth of the Mission River were all below detection limits for 2378-TCDD.

The numbers given above for residues in fish represent 2378-TCDD which is the chemical of greatest concern. The data of Stalling et al. (1983) for Great Lakes fish suggest that if 2378-TCDD is detectable, there will be on the average about twice as much 2378-TCDF, and 9 times as much total chlorinated dioxins and furans. Of course that will vary with different sources which provide different proportions to the environment. Bearing in mind the relative toxicities, 2378-TCDD appears to be the major contaminant.

Birds and other predatory animals are eventual recipients of bioaccumulative substances. Numerous examples with insecticides and other chemicals in recent decades have shown that fish-eating birds are particularly susceptible. In the last few years there has been concern in several parts of the world including the Great Lakes, that PCDDs and PCDFs may be playing a significant role in reproductive failure of certain groups of birds. The latest flurry of concern came from British Columbia in the autumn of 1987 when it was reported that a colony of Great Blue Herons had failed to hatch a single chick from 60 nests. The colony was very near a pulp mill. Newspapers saw the situation as clear-cut ("Wipe-out of heron eggs

linked to dioxin"), but in fact the birds had been successful the previous year (1986) with extremely high concentrations of PCDDs. Whether bioaccumulative toxicants or predation by crows, the residues in heron eggs were indeed high. The 1986 concentration of 2378-TCDD averaged 90 ppt, and expressing all the forms as their toxic equivalent of 2378-TCDD (TEQ) would give a value of 190. The "fingerprint" of the PCDD distribution suggested a source that was primarily chlorophenol preservatives (Philip Whitehead, Canadian Wildlife Service, Delta, B.C., personal communication). Other possible effects on birds have been summarised in MOE (1985), but the missing link in assessing most situations is absence of any proven correlation between residues in the body and the deleterious effects.

10.4 Risk Assessment from Laboratory Studies with Mammals

SUMMARY. Exposure of humans to chlorinated dioxins and furans has caused severe skin eruptions ("chloracne"), but there is not enough clear evidence of chronic effects to estimate the allowable exposures directly. Experiments with mice, rats, and other animals indicate a no-effect level of 1 ppt of body weight per day (ng/kg.d) for various sublethal effects. Since these substances do not seem to be genotoxic (mutagenic) they are considered promoters of cancer, but not initiators. A safety factor of 100 predicts an acceptable daily intake (ADI) of 0.7 ng 2378-TCDD/day for a 70-kg human. That ADI may be overly conservative, considering (a) that it is an extremely small fraction of the intake that causes acute effects in humans, (b) that it is much lower than the apparent ADI in some other mammals, and (c) that the observed acute/chronic spread is not so great in other mammals.

In contrast to the paucity of toxicity studies with aquatic organisms, there have been many laboratory studies of toxicity to mice, rats, etc., as well as epidemiological studies in humans. Some of these go back 30 years and it has been estimated that total direct cost of toxicological research on chlorinated dioxins and furans has been one hundred million dollars.

Risk assessment among mammals is almost always for the purpose of protecting human health, and this process may be considered to have a number of components.

1. **Hazard assessment.**

   a. Hazard identification. This is the determination of the degree of toxicity or danger posed by a substance. Identification could involve toxicity tests with laboratory animals, or study of diseases in groups of humans exposed to the substance in the work place.

   b. Dose-response assessment (Hazard estimation). This establishes the relation between the degree of exposure or the amount taken into the body, and the degree of deleterious effects produced. Ideally the studies should cover low doses and their subtle effects, since those are most relevant for deciding "safe" levels for humans.

2. **Exposure assessment.** This involves measurement of the actual or probable exposures that humans may encounter or have encountered.

3. **Risk characterisation.** This combines the previous items since there is an attempt to estimate the frequency of health effects in humans, from the levels to which they may be exposed. This ends the assessment, but the results may then be used in a regulatory way to decide on "acceptable daily intakes" for people, and/or allowable levels in the work place or in food.

The only direct experiments on humans involved application to the skin of volunteer prisoners. Severe chloracne, resulting in scars, was caused in 8 out of 10 volunteers by 100,000 ng applied to the skin. However, there were no other symptoms, and 8,000 ng applied twice did not have any apparent effect among 60 volunteers. The study was done about 1965, but unfortunately the volunteers were not followed to check for any longer-term effects.

There has been an adequate number of studies with 2378-TCDD and laboratory animals. The lethal dose of 2378-TCDD is remarkably variable between species. Although guinea pigs are killed by a single dose of 600 ppt (i.e. 600 nanograms per kilogram of body weight) the comparable lethal dose in hamsters is almost 2,000 times higher at 1,160,000 ppt. (Still the substance is as toxic to hamsters as the deadly insecticide Parathion.) Monkeys are killed by a dose of less than 70,000 ppt body weight. The mechanisms causing death are not understood but involve "wasting away" for a couple of weeks, perhaps because of problems involving vitamin A, or interference with thyroid activities, the dioxins being quite similar in chemical structure to two of the thyroid hormones. For comparison, the Acceptable daily intake (ADI) for humans is 0.01 ng.kg, lower by a factor of 7 million that the lethal dose for monkeys.

Laboratory studies on carcinogenicity developed after 1969, when the herbicide 2,4,5-T appeared to have powerful action as a teratogen (causing defects which show in newly-born animals). The teratogens were actually the contaminating polychlorinated dioxins, with no-effect levels of 100 ng/kg.d (nanograms per kilogram of body weight per day). Since then it has been demonstrated that 2378-TCDD causes significant liver cancer in female rats at dosages down to 10 ng/kg.d for long-term exposure (essentially lifetime) although total tumours in all organs were fewer than among control rats (Kociba et al. 1978). Dosage of 1 ng/kg.d did not cause such an effect, and neither 1 nor 10 ng/kg.d caused a significant increase in any kind of tumours in male rats. Similar results were obtained for rats by NTP (1982) with some erratic findings but an apparent no-observed-effect level (NOEL) of 1.4 ng/kg.d. In mice the carcinogenic thresholds were higher, with NOEL of 7 ng/kg.d in males and 30 in females (NTP 1982).

It required higher concentrations of hundreds of ng/kg.d or more to cause birth defects (teratogenicity) or effects on embryos and fetuses in mice and rats. Doses in the tens of ng/kg.d were enough to cause teratogenic effects in monkeys and to affect reproductive capacity of rats (summarised in MOE 1985).

The carcinogenic potential is usually taken as the aspect of most concern for protection of humans.

The mechanism by which 2378-TCDD is assumed to cause cancer is of great importance in estimating the numerical value of a "safe" level. It is generally considered today that many or most cancers involve toxicity to a gene, specifically, mutagenicity or damage to the DNA which determines the activities of the cell and passes the heritable instructions on to daughter cells. Many chemicals have such a genotoxic action, and they are potential or actual initiators of cancer. There is no really safe level for an initiator; as exposure becomes lower, the frequency of genotoxicity becomes less but never becomes zero. Therefore there can be no "acceptable daily intake" for an initiator of cancer. Regulators often substitute the "virtually safe dose" (VSD) which is usually taken as the amount that is estimated to cause only one case of cancer among a million people exposed to such a level for a lifetime. If the estimation is to be based on lab tests, there are various models that allow one to start with, say, a dose that affected one mouse in ten, and predict to the dose expected to cause an effect in one mouse in a million. Sometimes it is simply calculated as a direct proportion, which in the example above would be the ratio one in a million to one in ten, or 1/100,000 of the dose that affected one mouse out of ten in the laboratory.

The chlorinated dioxins in general are not thought to be in the category of initiators, and in fact numerous tests have shown no conclusive evidence that 2378-TCDD is a mutagen (Tschirley 1986). The potential for mutagenic activity has not been disproved, but it failed to show up conclusively in 11 types of tests (NCASI 1987a). However, 2378-TCDD and many other substances are considered to be promoters, and greatly increase the likelihood of a tumour if DNA has already been damaged by spontaneous or chemical-caused action. Promoters of cancer are more similar to the ordinary non-carcinogenic toxic substances, which have some lower "threshold" of dose or concentration that causes no apparent damage. Apparently the cells exposed to low levels of such promoters can deal with the chemical routinely, or they can repair any damage after exposure has ceased or paused. Thus a NOEL is apparent in the laboratory experiments, and is used in estimating an Acceptable Daily Intake (ADI) for humans. After an appraisal of the literature, we have used that approach, the same one selected by MOE (1985) and NCASI (1987a). A recent publication by Greenpeace (Van Strum and Merrell 1987) argues forcefully that there are no doses of 2378-TCDD in laboratory tests that do not cause ill effects, and that the "no-threshold" model should be used to evaluate risk, but we do not feel that approach is warranted. The actual mechanism by which 2378-TCDD acts as a promoter of tumors is not known although there are many hypotheses.

The body's defence against polychlorinated dioxins is similar to that for some other toxicants such as polyaromatic hydrocarbons (PAH). The body produces certain enzymes, chiefly in the liver, as a response to the presence of the toxicant, and the enzymes metabolise it to less harmful forms which can be excreted. There are families of these enzymes, variously called by different workers "mixed function oxidases", "P-450 enzymes", or "aryl hydrocarbon hydroxylases (AHH)", and they can metabolise a vast array of substances that are harmful or foreign to the body. Their production is triggered when a toxicant, say 2378-TCDD, combines with an "AH receptor", and that new combined molecule acts to turn on specific genes which cause the production of the P-450 enzymes. The chain of events is reversible and the enzymes decrease when the toxicant is no longer present. The enzymes can be measured and their presence is sometimes used as evidence that a toxicant is or was present in a test-animal. The technique of measuring the stimulation of P-450 enzymes has been used as one way of estimating the relative toxicity of the various categories of chlorinated dioxins and furans.

The Acceptable Daily Intake by humans of a toxicant (one that is not an initiator of cancer) is usually estimated by applying a safety factor to laboratory work with animals or epidemiological surveys of humans. The magnitude of the safety factor depends on the type of data available.

> **A safety factor of 10** may be used if there is good data available from humans exposed chronically (lifetime), i.e. the ADI is 1/10 of the NOEL. This is essentially to allow for sensitive individuals in the population.
>
> **A safety factor of 100** is often used if there is good data for chronic exposures of animals, the extra order of magnitude being intended to allow for differences between species (e.g. mice to humans).
>
> **A safety factor of 1000** is often used if information comes from somewhat uncertain chronic tests or from short-term exposures of animals, the further factor of 10 being an allowance for the difference between short and long exposure.

Sometimes the NOEL is not clearly established. The allowable level is sometimes estimated on the basis of the lowest observed effect-level (LOEL), allowing a further safety factor of 2 to 10.

The human ADI for 2378-TCDD may be estimated by applying the appropriate factor of 100 to the mice and rat NOELs mentioned above. Thus our estimate of an ADI for humans would be 1 ng/kg.d x 1/100 = 0.01 ng/kg.d. For a 70-kg human, the total daily dose thought to be "safe" would be 0.7 ng. This is the same estimate of ADI derived by NCASI (1987), and by MOE (1985) based on the work of Kociba et al. (1978) and Murray et al. (1979). In the US, the Environmental Protection Agency and other agencies have adopted, as a matter of policy, the "no-threshold" model and estimated much lower numbers for daily intake. A powerful argument is made in the review by NCASI (1987a) that the US approach is not warranted in the case of 2378-TCDD, and we agree with NCASI on that point. (According to a news report in December 1987, US EPA finally changed its mind, and raised its estimate of the ADI.) We recommend the ADI of 0.01 ng/kg.d as a perhaps cautious, but useful guideline at this time.

10.5 Epidemiological Studies

Humans have been exposed to polychlorinated dioxins and furans in the work place, by accidents, and by herbicide spraying. As outlined below, there are some rather nebulous conclusions about deleterious effects and the dosages causing them. The allowable intake for humans is best estimated by the animal experiments summarised above.

Skin eruptions called chloracne are the most consistent documented effect in humans. The first documentation of a PCDD problem followed an outbreak of chloracne in a factory in Germany in 1957; 2378-TCDD was identified as a contaminant of trichlorophenol, used in manufacture of pesticides, particularly the herbicide 2,4,5-T. Since then, contamination from polychlorinated dioxins has been reduced in such chemical plants, although not eliminated. Other major problems and/or studies have involved accidents at factories in at least ten other countries, contamination of the soil in Times Beach, Missouri, by spraying contaminated chemical factory waste and oil for dust control, a major explosion in a chemical factory in Seveso, Italy in 1976 with widespread contamination in a downwind plume, spraying of herbicides ("Agent Orange") in Vietnam, and occupational exposure to herbicide spraying in agriculture and forestry. There are more than a dozen intensive studies of direct exposures involving some thousands of people. More diffuse studies (agricultural and forestry workers) involve tens of thousands of people. There was the above-mentioned deliberate experiment with volunteer prisoners.

What emerges from those many studies is that moderate to heavy exposure to PCDDs causes chloracne and some other abnormalities of the skin such as excessive hair. The chloracne has been clearly demonstrated for occupational exposure at many places, for the Seveso explosion, and in Vietnam. However, even among more than a thousand workers who had high exposure as was clear from chloracne and other evidence, there is no consistent picture of more subtle effects such as cancer, heart disease, reproductive problems, or premature death in general. There may indeed be such effects, and some have been found to be statistically significant in one study or another, but if so, the same effect was not documented in other parallel studies, or is suspect for one procedural reason or another. Many of the studies lacked proper control groups of people selected to match the exposed group.

This generalisation of lack of documented effect may conflict with the reader's impression from television documentaries and newspaper accounts but nevertheless seems to be warranted. For example the appreciable exposure of several thousand people in the Italian explosion was severe enough to cause 184 cases of chloracne. It has generated tales of spontaneous abortions and malformed babies but examination of the data is anything but conclusive, and statements of abortions apparently involve religious mores and trips to Switzerland. Another well-known example is the case of the "Ranch Hands", 1,200 US

soldiers who sprayed herbicides in Vietnam. They have been and are being followed by military doctors but there is no evidence of increased mortality or morbidity during the 20 years since the peak of spraying activity. Complaints of the veterans were finally settled out of court for $180 million although within the court the judge said that health effects had not been demonstrated. A much more difficult question is whether effects occurred among Vietnamese people who were subjected to spraying. There are reports from conferences in Vietnam of high rates of defects in newborn children, but such reports have not been published in the open scientific literature to allow for peer evaluation. Some attempts to rate the incidence of birth defects in Vietnamese hospitals were flawed by the preponderance of city people rather than the exposed rural people, and by the poor records of normal incidence of defects. In particular, investigators were on the lookout for increased incidence of cleft palate and similar malformations of the mouth, because of the results of laboratory tests on rodents, but such defects were not documented.

Some statistically significant effects from one or other of the studies may be mentioned. (1) People who lived in a trailer park at Times Beach, Missouri, where contaminated oil was used for dust control, show serious impairment of the body's immune system, which has the function of protecting from infectious agents. The effect has been noted in many studies with animals, and is associated with a loss of lymph tissue. Therefore it was surprising that the impairment in Times Beach people was not accompanied by increased morbidity or mortality, and has not been documented in other human studies. (2) An association between increased soft-tissue cancer and degree of exposure to herbicides was shown in Swedish workers. The results cannot be directly attributed to PCDDs because of the great mixture of chemicals included in the exposures. (3) Liver damage, as measured by various tests of liver enzyme function, was seen in at least 3 locations among some of the workers who showed chloracne, and was also documented following the Seveso explosion, and among Americans who had sprayed agent orange. Liver damage also shows up in most sublethal studies with laboratory animals. (4) Damage to the nervous system has been evident in several of the more severe exposures of humans, mostly in the peripheral nerves, with loss of sensation. For each of these items, there were other studies which failed to find such effects.

10.6 Chlorinated Dioxins in Waste Sludges from Kraft Mills

SUMMARY. Concentrations of chlorinated dioxins and furans in the sludge of waste treatment ponds vary by a factor of 100. The median TEQ (Toxicity EQuivalent of 2378-TCDD) may be about 70 parts per trillion. The bleach plant in kraft mills contributes almost all of the PCDDs and PCDFs. Their major destination can be in the bleached pulp, the sludge of waste treatment, or the liquid effluent, depending on the mill, but all three outputs are potentially important.

Since any polychlorinated dioxins and furans in mill effluent would travel with particles, they would be expected to show up in the solids at the bottom of clarifiers or ponds used for primary and secondary treatment. That sludge is periodically removed and is customarily dumped on land, another example of there being "no place to throw things away". However it seems likely that the PCDDs might stay with the particulate matter of sludge rather than travel with groundwater that could reach wells. That supposition fits with a measurement of leachate from a sludge disposal site near Fort Frances; no chlorinated dioxins or furans could be measured, despite a claimed detection limit of 0.02 ppt for 2378-TCDD (MOE press release, July 17, 1986).

Table 10.2 Measurements of chlorinated dioxin and furan in samples of sludge from waste treatment facilities of bleached kraft pulp mills. Only the two important chemicals are listed. The 2378-TCDF for Ontario mills may include other isomers of tetrachlorinated dibenzofurans. NM = Not Measured. TEQ signifies total Toxicity EQuivalent in terms of 2378-TCDD. Two of the mills in the group of 6 US mills are also included in the group of 5, but for a different time of sampling. The US data are for combined primary and secondary sludges.

	Concentration (Parts per trillion)			
	2378-TCDD	2378-TCDF	TEQ	Source
Ontario	210	NM?	-	MOE May 1986
Ontario	<20-100	<37?	-	MOE July 1986
	<20-100	<37?	-	
	<20-100	37	-	
	<20-100	260	-	
	<20-100	280	-	
	<20-100	1100	-	
5 US mills	3.3-180	34-760		Amendola et al.
	average 56	average 370	average 93	1987
	median = 37	median = 330		
6 US mills	17	300	48	Amendola et al.
	37	200	60	1987.
	53	280	81	
	150	880	255	
	190	760	270	
	240	2300	500	
Wisconsin	3.5	NM		Van Strum and
	128	NM		Merrell 1987,
	159	NM		p. X-13, citing
				US National
				Dioxin Study,
Maine	17	NM		through a memo
	32	NM		of H. Zar 1986
	51	NM		
Average	99*	640*		153
Median	53*	290*		

* Average excludes the 5 US mills.

Measurements have been made on sludges from the waste treatment systems of 7 Ontario bleached kraft mills (MOE, press releases, May 2 and July 17, 1986). As shown in Table 10.2, one of the sludges had 2378-TCDD but the others had concentrations below the detection limits of 20 to 100 ppt. Two of the sludges apparently had no detectable concentrations of the other chlorinated dioxins and furans assessed. "Tetra furan" was present in the other 4 samples, at remarkably varied concentrations. The sludge with the

high tetra furan also contained 360 ppt of hepta-CDD, 1800 octa-CDD, and 350 octa-CDF, all of slight toxicity. The identification of the substances is not precise enough to estimate the Toxicity EQuivalents of 2378-TCDD by the method given above. Measurements are also available from US mills and are shown in Table 10.2.

The most striking thing for measurements of the two chemicals in the sludge of 5 US mills is the variation from mill to mill. Values for 2378-TCDD range from 3 to 240, and from 34 or less to 2300 for 2378-TCDF, in each case spanning two orders of magnitude. It is clear that one must be cautious about referring to an "average" or "typical" bleached kraft mill insofar as levels of PCDDs and PCDFs. Averages or median values might be used for some purposes as long as the 10-fold variation above and below were kept in mind. Some such central values are indicated in Table 10.2. Subjectively, it appears that overall median values might be in the vicinity of 40 ppt 2378-TCDD, and 300 ppt 2378-TCDF. Median TEQ might be in the vicinity of 70.

On the average, sludges appear to contain about 8 times as much furan as dioxin. From 53 samples of sludge and various streams within 5 US mills, Amendola et al. (1987) conclude that the ratio TCDF/TCDD is fairly consistent within certain mills, but highly variable from mill to mill, and indeed their average ratios for the 5 mills ranged from 2 to 15, and the overall average was 7.7. Sludges from the 6 US mills in the table show a similar variation in ratios, from 4 to 18 with an average of 8. Assuming the TEQ of 0.1 for 2378-TCDF, the two chemicals rate about equal in contribution of toxicity.

One concern about chlorinated dioxins in sludge would not seem to exist in Ontario. The material is used in some regions as soil dressing for agriculture or lawns. A hypothetical example was set up by NCASI (1987) in which a farmer used sludge as soil dressing for many years, grew crops and cattle, and used his own products as food. The estimate produced a safety margin of 500 for the ADI.

10.7 Sources, Fates and Amounts in Bleached Kraft mills

The 5-mill US study provides confirmation that the bleach plant is the major source of CDDs and CDFs in bleached kraft mills (Amendola et al. 1987). Disregarding one anomaly, the bleach plant contributed 70% to 100% of the totals found in mass balance calculations. Waste stream from the caustic extraction stage had the highest concentrations, averaging 1.7 TEQ ppt, while those from the chlorination stage had only 0.14 TEQ. The hypochlorite stage produced 0.63 TEQ, and chlorine dioxide stages were very low but could not be averaged.

The kraft pulping process did not produce measurable 2378-TCDD, although traces of 2378-TCDF were occasionally found. Chlorinated dioxins and furans were seldom detectable in the water supply taken into the mills.

After bleaching, there were PCDDs in the pulp from most mills. However, the mass balance of the contaminants between the bleached pulp and the bleach plant wastewater was extremely diverse. In one mill, mass balance calculations showed 100% of the chlorinated dioxins in the water and none in the pulp; in two of the seven other cases studied, there was more in the pulp than in the wastewater.

Amendola et al. (1987) proceeded with their mass balance calculations and compared the outflowing liquid effluents with the sludges that settled in waste treatment ponds. Again the proportions were consistent within mills but extremely variable between mills. Sometimes almost all the contaminants were in the sludge rather than the liquid effluent, and sometimes it was the other way around. They assumed, but did

not measure, that there was little aerial escape, i.e. from stacks. (Slight concentrations of some less toxic PCDDs and PCDFs have been recorded in stack gases of one mill according to Van Strum and Merrell (1987).)

The fate of 2378-TCDD and 2378-TCDF was then tabulated by Amendola et al. (1987), by taking bleached pulp into the mass balance calculations. Table 10.3 simplifies their numbers by combining the percentages for 2378-TCDD and 238-TCDF, since they were almost identical.

Table 10.3 Distribution of chlorinated dioxins and furans in outputs of US bleached kraft mills. (from Amendola et al. 1987).

Mill	A	B	C	D	E	Average
Bleached pulp	19%	51%	30%	30%	56%	39%
Wastewater sludge	16%	18%	68%	70%	22%	39%
Liquid effluent	64%	21%	2%	0	22%	22%

The proportions were again extremely variable between mills. The pulp contained anything from 19% to 56% of the PCDDs and PCDFs leaving the mill. The sludge and effluent traded back and forth as carriers of major portions of the contaminants. The average values shown in the tabulation mean very little, except to show that all three carriers must be regarded as significant.

Amendola et al. (1987) also reported concentrations and amounts discharged. Variation was 1 to 2 orders of magnitude for the various mills, but perhaps we may take the averages as a general idea of values. The numbers in the following tabulation are averages expressed as TEQs, i.e. Toxicity EQuivalents of 2378-TCDD.

	Liquid effluent	Wastewater sludge
Concentration, parts per trillion TEQ	0.094	93
Mass loading, milligrams per day	11	6.9
Mass flow, nanograms/ADt pulp	40	

The average mass loading in the effluent is 11 mg/d which is higher than in the sludge. The average concentration in sludge is a little higher than the value of 70 ppt that was hazarded as an estimate of the median, in the previous section.

10.8 Perspectives and Suggestions about PCDDs and PCDFs in Pulp Mills

SUMMARY. (1) An average bleached kraft mill might produce 11 mg per day of 2378-TCDD (TEQ) in the liquid effluent. That is much less than the average of 520 mg/d TEQ from a municipal garbage incinerator in Ontario in the early 1980s. Sludge from municipal waste treatment plants may be higher than sludge from bleached kraft mills. Direct intake by humans from paper products would appear to be trivial. (2) However the outputs of PCDDs and PCDFs by mills could have an appreciable impact and should not be ignored. The average loading per day from a single mill could be enough to kill three people if it were all taken in by those people, or it could equal the estimated Acceptable daily intake (ADI) for 16 million people. Assuming that all of a day's contaminants were taken up by fish, that would bring a quarter of a million big fish up to the maximum level for human consumption. Intake of chlorinated dioxins from fish could be potentially the most important source for some people in Ontario who ate fish daily, under worst-case conditions. (3) Bleached kraft mills should accordingly be taken as potentially important sources of chlorinated dioxins. Still the risk should be kept in perspective, since the estimated ADI, continued for life, may be equivalent to one chest x-ray. (4) Although we assume that reduction in chlorine use in a mill would reduce the production of chlorinated dioxins and furans, and some recent evidence supports that theory. (5) We fear that media publicity may divert energies from productive avenues of pollution control into blind alleys of ill-conceived, very expensive and routine surveys of "dioxin" concentrations. (6) If a battery of toxicity tests is to be used to assess mill effluents, it should be recognised that the usual tests of genotoxicity (e.g. the Ames test) will not show effects of chlorinated dioxins and furans.

In this section we attempt to juxtapose various bits of knowledge on chlorinated dioxins and furans, to evaluate problems and non-problems, and express some of our views on desirable approaches.

10.8.1 Dioxins are not a Brand New Problem

The spate of reports of chlorinated dioxin(s) in new places does not necessarily represent recent "pollution". In the last few years, chemical detection limits have moved much lower, and are now in the low parts per trillion range or better. Chemists can now measure levels in the environment that have probably been present for some time.

10.8.2 Overly-Conservative Value of ADI?

The amount of 2378-TCDD on human skin which caused acute chloracne was 100,000 ng as a single dose, and that is 140,000 times higher than our lifetime ADI of 0.7 ng/d for a 70-kg person. That is a very wide spread, and suggests that our ADI is overly-conservative. For example the ratios of acute/chronic effects on laboratory animals would be in the vicinity of a few hundred to a few thousand (MOE 1985, Table 3.2.2B). The conservative nature of this ADI is also suggested by the wide spread in acute/chronic numbers in examples given below in Section 10.8.3.

For comparison with the ADI of 0.01 ng/kg.d, a "safe" daily intake for cattle and goats has been diagnosed as less than 4,000 ng/kg.d (MOE 1985), i.e. as much as 40,000 times higher. The MOE document also says (p. 3-139) that "... observations suggest that man is no more sensitive to 2,3,7,8-T4CDD [2378-TCDD] than rats or mice." The safety factor of 10 allowed for the species jump to humans may be overly-cautious. In protecting human health, allowable intakes must, of course, be cautious. That is why we have agreed with the cautious recommendations of MOE (1985) and NCASI (1987a).

The actual intake of PCDDs and PCDFs by Ontario residents has been estimated in a preliminary way by MOE (1985), judging from residues found in human tissues. The estimate is 0.007 ng/kg.d or 0.5 ng/d for a 70-kg human. If correct, the value is 70% of the ADI used here.

10.8.3 Magnitude of "the Dioxin Problem" at Pulp Mills.

A single pulp mill would apparently be a less significant source of chlorinated dioxins and furans than a single municipal garbage incinerator; such an incinerator might equal the output of 36 kraft mills. An average of 11 mg/d of TEQ was given above as the 5-US-kraft-mill average for the liquid effluent, not including the sludge. This is much less than the average of 520 mg/d TEQ estimated as the average of two for municipal incinerators in Ontario in the early 1980s (MOE 1985). The estimates for the garbage incinerators are considered realistic, according to more recent unpublished checks on emissions (personal communication, V. Ozvacic, Ministry of the Environment, Toronto, Ontario).

Similarly, kraft mills may not be a more serious contributor of these contaminants than is municipal sewage. Measurements at the Hamilton water pollution control plant indicate 92 ppt TEQ in the sludge (MOE 1985, p. 4-107) which is somewhat higher than the median TEQ of 70 estimated for 5 US bleached kraft mills (Table 10.2, 37 ng 2378-TCDD/kg and 330 ng 2378-TCDF/kg).

An attempt to estimate the total input of PCDDs and PCDFs to the Ontario environment, in terms of TEQs, was made by MOE (1985, Table 4.2.5.B), with acknowledgement of many unknown contributions. We have generalised their estimate as:

32 kg from non-municipal combustion (vehicles, fires);
9 kg from municipal burning;
6 kg imported from other places (e.g. Niagara dump sites);
4 kg as contaminants of chlorinated phenols; and
a trivial amount from herbicides.

Thus the incomplete tally is about 50 kg/yr. If we take the average mass discharge in liquid effluents from the 5 US kraft mills (Amendola et al. 1987), and express as TEQ using the same factors recommended by MOE (1985), the average per mill is 12 gm/year of the MOE TEQs. Assuming that average value applies to the 9 Ontario kraft mills, we have only 110 g/yr TEQ, or something less than one four-hundredth of the contribution from other sources. The comparison is very rough but certainly suggests that pulp mills should not be singled out as the major source of these substances in the environment.

We cannot venture many comments on the human health risk from PCDDs and PCDFs in paper products, a topic which was an issue in the media in autumn 1987. A proper risk assessment requires knowledge of how much of the chemical gets out of the paper product and into the consumer, and must consider total intake from all sources. A rough exploration may be made. The CBC television show "Market Place" on Dec. 8, 1987, reported their own tests with paper products. The highest value among 5 products was for paper towels, and it was 20 parts per trillion, expressed as equivalents of 2378-TCDD (TEQs). If the acceptable daily intake (ADI) is 0.7 ng for a 70-kg human, then that amount would be contained in 35 grams of paper towels, which is 12 squares of towel from a standard kitchen roll. Of course a consumer is not going to eat and digest the towels and take all of the chlorinated contaminants into the body. How much comes out of the towel and into the consumer? One percent? A thousandth of one percent? We do not know, but considering the potential transfer mechanisms, the fraction would probably be very low. If 1% were transferred it would mean 1200 towels a day to be used, while the smaller percentage would

mean 1.2 million towels a day to be used, for the consumer to get an ADI from that source. Of course, other sources would have to be considered.

For human exposure we defer to the Federal-Ontario Ad Hoc Working Group on Multi-Media Standards, which will no doubt carry out a complete risk analysis in order to finalise its acceptable levels of PCDDs and PCDFs in food. The working group was awaiting some results that were due in December 1987. The American Paper Institute, in a press release of December 18, 1987 concludes from undescribed tests that concentrations of these contaminants in paper products would have to be several orders of magnitude higher (hundreds to tens of thousands of times?) to cause an intake that would still be considered a virtually safe dose for people.

Appreciable amounts of chlorinated dioxins and furans leave the mill with the liquid effluent, if we consider them as potential residues in fish or in terms of human ADI. The average mass loading in a study of 5 US mills (Amendola 1987) for liquid effluent was 11 mg/d as TEQ, which is 11,000,000 ng. Let us populate the river downstream of this "average loading" with hypothetical 2-kg bass, and assume that all the chlorinated PCDDs and PCDFs magically get into the fish and reach the Canadian limit of 20 ppt (on a TEQ basis). We would need 275,000 bass to use up the day's production of contaminant, which is a lot of good-sized fish!

If a human ate 300 gm of these bass in a day, quite a decent portion of fish, he/she would take in 6 ng (TEQ) which is more than 8 times the ADI of 2378-TCDD that we would recommend for continued intake.

We grant that none of those scenarios would happen, but they provide some comparisons of the numbers involved. It appears that PCDDs and PCDFs from bleached kraft mills should not be arbitrarily dismissed as a trivial problem.

The potential contamination of fish by bleached kraft mill effluent emerges as a significant question, since eating contaminated fish could provide one of the biggest sources of PCDDs and PCDFs in total intake of a human. A Ministry report (MOE 1985, p. 5-20) has estimated some worst-case scenarios for Ontario residents, and consumption of fish is the largest potential source of intake. Their estimates are listed below, and it must be repeated that they are worst-case, and no single person would encounter all the separate intakes. Values are taken as a proportion of an ADI of 0.7 ng/d for a 70-kg human. The intake from fish assumes that TEQ of residues in the fish is 20 ppt which is the maximum limit for consumption in Ontario. However, the intake of fish is taken as the Canadian average of only 14 g/day, (a tablespoon of fish), so the picture would be quite different for frequent fish-eaters (see three paragraphs above). The polluted air would be in the plume of an incinerator, as would be the contaminated soil, and the water would be like the surface water from the lower Niagara and therefore unrepresentative of actual Ontario drinking waters which do not have detectable amounts of chlorinated dioxins and furans.

Worst-case source	Daily dose as percentage of recommended Acceptable daily intake
Fish at maximum allowed residue level	40%
Air near municipal garbage incinerator	19%
From fat in meats	9%
Contaminated water, as if for drinking	0.4%
Dermal sorption from contaminated soil	<0.1%
Additional from soil, for children	<1.7%

10.8.4 Other Risks; Blind Spots and Fads in Toxicants

Further perspective may be added by comparing with other risks. Safe doses for humans are often estimated as the lifetime exposure that would increase the risk of mortality by one chance in a million, and the ADI that we suggested for 2378-TCDD might have that implication but is probably safer. For comparison, it has been estimated that the chance of death would be raised by one in a million if any one of the following were done (Slovic 1986, Whyte and Burton 1980):

smoking 1.4 cigarettes;
travelling 80 km by automobile;
canoeing for 6 minutes;
living for 2 days in Boston (air pollution);
one chest x-ray; or
drinking 30 diet soft drinks (saccharin).

B.N. Ames, after whom the Ames mutagenic test is named, is credited with some interesting views in written testimony to a committee of the California senate (Goodings 1987). "The main current fallacy consists in thinking that carcinogens are rare and that they are mostly man-made. My own estimate is that over 99.99% of the carcinogens Californians ingest are natural (e.g. natural toxic chemicals in plants, mold carcinogens) or traditional (e.g. cooking food, smoking cigarettes, alcohol)." Considering the current public concern about 2378-TCDD in coffee filters, it is interesting that Ames points out that coffee contains about 4,000,000 ppt of hydrogen peroxide and 4,000,000 ppt of methylglyoxal which is a carcinogen. (There are about 4 cups to the litre.) Similarly, Ames estimated that cola contained the carcinogen formaldehyde at 18,000,000 ppt.

10.8.5 Origin of the Unchlorinated Dioxins?

The bleach plant is the origin of chlorinated dioxins and furans in bleached kraft mills. The source of the precursors has not received much attention. Obviously the requisite chlorine comes from the added chlorine and chlorine-containing substances. It is not clear whether the unchlorinated dibenzo-p-dioxin and dibenzofuran precursors are derived from the components of the pulp or from the process water. The uncertainty is because all the chemical studies concentrate on chlorinated molecules. Few of those are found in the intake water, for example, but there might be a good supply of unchlorinated dioxins and furans in the water; no-one attempts to measure them so we do not know their concentration. Similarly in the controversy about forest fires as a source of dioxins, investigators concentrated on chlorinated dioxins in smoke, sediments, etc., and it is generally conceded that their levels are low. However, it is possible that forest fires could be a major source of unchlorinated dioxins, which might travel with particles in surface water into the mill, then become chlorinated. It has been pointed out, for example, that high concentrations of chlorinated dioxins in the sludge of a bleached kraft mill in Fort Frances correspond to a heavy incidence of forest fires in the vicinity, while low levels in sludges of mills at Prince Albert, Saskatchewan and Abercrombie Point, Nova Scotia correspond to light incidence of fires (J.L. Betts, Environment Canada, personal communication).

The source of the precursors, unchlorinated dibenzo-p-dioxins and dibenzofurans, would be of importance if there were ever any attempts to reduce the chlorinated forms in mill products as a particular project, divorced from general decrease in use of chlorine. (We do not recommend that approach.)

10.8.6 Does Reduction of TOX Mean Reduction of Chlorinated Dioxins?

A topic related to item (5) is the lack of information on whether a general reduction of chlorine use in mills (lowering TOCl in effluent) would proportionally reduce particular components such as PCDDs in the wastewater and products. The wide variation in CDDs and CDFs among mills might provide clues, if that variation could be correlated with the particular sequences and proportions of the bleaching processes.

One study (Consolidated Papers Inc. 1987) on one bleached line indicated that the installation of an oxygen delignification stage reduced the discharges of 2378 TCDD to non-detectable levels which corresponded to 90% or more reduction, according to the assumptions one makes about the true value of a "non-detectable" concentration. We have received a little unpublished data which indicates that high levels of chlorine dioxide substitution have a comparable effect. **While these data indicate that there is a possibility that 2378 TCDD can be essentially eliminated by one or both of the latter process modifications, it would be premature to assume that this will be effective in all mills. Ongoing work by NCASI, EPA and MOE will make considerably more data available during 1988.**

It is somewhat worrisome, for example, that by far the highest levels of TCDFs, hepta-, and octa-compounds in sludges at Ontario mills (Table 10.2) were at the mill which has a low level of chlorination because of its oxygen delignification stage. The mill explains that the organochlorines are sorbed onto carbon which is added to the effluent as boiler ash, then settles as part of the sludge. Still the example is a warning about leaping to assumptions on the subject of reduced use of chlorine. It is possible that some of the "tetra furans" reported by the Ministry of the Environment may be in part a mistaken chemical measurement of something else, for example chloroxanthenes and chloroxanthones which are found in sediments near Swedish mills, and are similar in structure to dioxins (Södergren et al. 1987).

Mill staff have speculated that the relatively high levels of TCDFs are due to the presence of flyash from the hog-fuel boiler, which contains elemental carbon in a partially activated form. It is well known that laboratory activated carbon absorbs chlorinated organic chemicals (it is the basis of most organochlorine analytical methods), so the foregoing speculation is not unreasonable

10.8.7 Profitable Directions in Scientific and Technical Endeavours?

We fear that the attention given by the press and the public to "dioxin" will stampede all of us, industry, government, and consultants, into paying too much attention to the wrong parts of this question and ignoring other more important things. We already see the initial stages of a giant and expensive phase of random monitoring and measuring of chlorinated dioxins and furans at pulp mills. At $ 1200 - $ 1500 per measurement, that could be a very expensive and long-lasting phase of discovering miscellaneous facts. Worst of all it could occupy the time and energy of key scientists, technicians, and regulators, without making any particular improvement in environmental quality. We have already heard of a large federal government chemistry laboratory in southern Ontario that is overwhelmed with samples for dioxin analysis, to the point at which no work can be done on other important projects. Scientists in particular have a great tendency to study such a toxicology question in great detail and government agencies tend to respond with a glut of sampling., instead of simply cleaning up the sources.

We urge industry and government to avoid any fuzzy, large-scale, routine or "baseline" surveys of chlorinated dioxins and furans. Small precise investigations could be launched if necessary to answer specific questions like the one above in Section 10.8.6. Elsewhere in this report we recommend a general decrease in chlorine bleaching and a consequent reduction in organochlorine discharges. Presupposing

the answer to Section 10.8.6, we assume there will be an associated reduction in chlorinated PCDDs and PCDFs. That is the direction to go, and each routine survey, each $ 1200 for a chemical measurement, only delays the journey or diverts it.

10.8.8 Regulatory Toxicity Tests

The conclusion that 2378-TCDD is not a mutagen has some relevance to suggestions for toxicity testing of kraft mill effluents. A popular and sensible approach today is to use "a battery of tests" to cover species differences and to cover different types of toxicity. An obvious candidate for any battery of tests is one for mutagenicity, such as the Ames test, with the objective of measuring potential carcinogenicity of the effluent. It is evident that chlorinated dioxins in an effluent might pass the test since they are not mutagenic, and yet the greatest concern expressed about 2378-TCDD is its carcinogenic quality.

11. GOALS

11.1 Rationale

Prior to the 1960's, there was little control of pulp mill effluent quality by regulatory authorities or the industry. Most Eastern Canadian mills discharged all bark and other wastes to watercourses, and the environmental effects were accepted as the cost of prosperity in an industrialised society. While there are few records, consideration of the pre-1960 operating practices indicates that kraft mill suspended solids discharges were in the order of 200 kg/tonne pulp produced (see Section 6.3.1), BOD was probably over 50 kg/tonne and all the effluents would have been toxic to fish in terms of current definitions.

As environmental concerns developed, Ontario kraft mills have effectively eliminated suspended solids discharges as an environmental problem. Discharges are in the range of 3-10 kg/tonne, and the material discharged is essentially non settleable, and does not create the sludge beds which were formerly characteristic of watercourses downstream of mills.

BOD discharges have been reduced, although not so spectacularly, and undesirably low levels of dissolved oxygen are limited to relatively short periods of the year. The recommendations in this report are intended to eliminate unacceptably low dissolved oxygen in receiving waters.

Toxicity to fish, according to the current standards, has been reduced, but not eliminated.

The existing criteria for characterising mill discharges were developed many years ago, and considerably more knowledge on effluent characteristics and environmental effects is now available. The concepts of BOD and suspended solids were developed in the early part of this century, and the fish toxicity criteria started coming into general use in the 1960s.

We feel that these criteria have to be re-evaluated, and have recommended modifications to the use of BOD and fish toxicity criteria. In view of the new knowledge available, and the progress made in improving effluent quality as defined by the above mentioned traditional criteria, we have recommended that regulatory emphasis should be shifted to persistent, bioaccumulative substances. In the kraft industry, these are mostly organochlorines (chlorinated organic compounds). While science has not defined the exact extent of environmental damage caused by these materials and the technology for chlorine-free bleaching is not yet proven, there is sufficient evidence for us to recommend that controlling regulations should be implemented.

Total Organically bound Halogen (TOX) is the most practical criterion for defining quantities of organochlorines, and we have recommended that mills be required to reduce TOX discharges substantially, on a schedule to be negotiated for each mill. This schedule must take account of the currently installed mill equipment since the proven and most probable technology involves modifications to the pulping systems which affect most parts of the mill process. Realistic schedules would be a few years.

While Swedish regulators have suggested longer term regulations to much lower levels of organochlorine, we consider that this should be evaluated as further knowledge becomes available in this rapidly developing field. We see no reason to expect that this initial move will prejudice future reductions in discharges of specific organically bound chlorine or of organochlorines in general.

11.2 Suggested goals

We offer a choice of four Levels of Achievement for pollution control and environmental protection in Table 11.1 so that the Minister can select the most appropriate level of environmental protection. This is a convenient framework for a number of reasons.

Firstly, it allows a rating of present status of effluent quality at the various Ontario mills, thus indicating where the earliest and maximal effort should be expended on improvement. Even within one mill there may be uneven levels of control for the different characteristics of the waste, for example there could be excellent control of suspended solids but an unsatisfactory level of toxicity. Such qualities may be rated independently for "level of achievement", again indicating where the focus should be for improvements.

Secondly, economic tags may be assigned to the four levels of achievement, and as discussed in Section 12. Thus the social and economic costs and benefits may be weighed along with the environmental considerations. We feel that the choice of a level of achievement is ultimately a function of the democratic process, and thus we have offered levels that we consider to range from unsatisfactory to very satisfactory at the present level of technology.

Finally, the four levels could be utilised to set a time-frame for future improvements. A suitable final goal could be selected and dates set for achieving milestones en route to that goal. As described elsewhere, the timing must in some cases allow appropriate lead-times to replace equipment at logical times, and for step by step integration of the new systems into the mill operating practices and processes.

We feel strongly that the Ministry must establish an even-handed treatment of mills in any such schedule. If an environmental protection program is to be effective, it must be visibly even handed, and we do not feel that was the case in 1987 when E.B. Eddy were prosecuted on an environmental matter, more vigorously than any other pulp producer has been in Ontario . This does not imply any approval of the soap spill which caused the extensive fish kill, nor do we suggest that the company should not have been prosecuted, **but we consider that it was counter productive to pursue so aggressively the kraft mill with the best quality effluent in the Canadian bleached kraft industry**. The implied message to pulp producers was that they should not bother to comply with environmental regulations, because the prospect of being prosecuted was not dependent on environmental performance.

We realise that the Ministry must uphold the law and that the Ministry cannot legally select who to prosecute on the basis of overall performance. However, we consider that the management of the environmental program is a responsibility of the Ministry, and that they must find a way to exercise commonsense judgement if the program is to succeed. This is a major challenge in view of the diverse circumstances that exist in the different mills.

Table 11.1 Levels of achievement for kraft component of pulp and paper mill effluents.

Level	BOD kg/ADt	SS kg/ADt	Site-specific DO in receiving-water outside mixing zone (NAS/NAE 1974)	Lethality of effluent for standard discharge volume of 175 m^3/t pulp	Sublethal toxic effect beyond the mixing zone	Organochlorines kg TOX/ADt
I	>30	>15	DO is at low level of protection or worse	LC50 < 50%	yes	$\geq$5.0
II	<30/16.5	<15	DO meets low level but not moderate level of protection	LC50 > 50%	yes	<4.5
III	<30/16.5	<10	DO meets moderate level of protection	LC50 $\geq$ 100%	none	<2.5
IV	<30/16.5	<10	DO meets high level of protection	LC50 $\geq$ 100%	none	<1.5

Abbreviations in Table 11.1. ADt: Air-dried tonne of pulp. BOD: Biochemical oxygen demand as measured over 5 days. DO: Dissolved oxygen. LC50: Median lethal concentration for rainbow trout in the Ministry of Environment static exposure. SS: Suspended solids. TOX: Total organically bound halides, in this case, mostly chlorine bound to organic molecules.

Column 1 shows "Levels of Achievement". Most people would probably consider that Level I was unsatisfactory for most of the columns. Nevertheless some mills would fall into that category for one or more of the conditions. One Ontario bleached kraft mill would meet all requirements for Level II, and almost those for Level III, and one of those levels would seem a reasonable goal for the immediately foreseeable future.

Column 2 deals with a release of oxygen-consuming waste, as measured by the classic BOD test. Canadian Federal regulations, for new or altered mills allow 16.5 kg per tonne for cooking and 13.5 for bleaching, thus 30 kg/t total for a mill producing bleached pulp. Where some or all of the pulp is unbleached, then the lower value of 16.5 kg/ADt unbleached pulp produced would apply.

Column 3 shows criteria for suspended solids.**Column 4** deals with site-specific dissolved oxygen (DO) in the waterbody receiving the effluent. Previously, there have been no particular regulations for this, but the requirement has nonetheless been implicit. Control orders appear to have been written to achieve satisfactory levels of dissolved oxygen. There is some pressure from industry to have site-specific requirements for DO or BOD, rather than an arbitrary level for the effluent. Obviously, the dissolved oxygen must be satisfactory if one wishes to have healthy populations of fish and other organisms, and therefore we are recommending minimum levels.

We have used the dissolved oxygen criteria suggested by the US National Academies of Science and Engineering (NAS/NAE 1974), criteria which are based on recommendations of Doudoroff and Shumway

(1970) and approved by the American Fisheries Society (Thurston et al. 1979). These recommendations allow certain depressions of dissolved oxygen, depending on both the level of protection selected and the "natural" minimum level of oxygen for the season, i.e. the level that would have prevailed historically with no pollution. The values may be taken from Table 11.2. for some circumstances, or calculated by the following formula, where M = Natural seasonal minimum dissolved oxygen in mg/L. A "floor" of 4 mg/L was established by NAS/NAE (1974), and we consider that it should be applied in Ontario, notwithstanding the foregoing.

High level of protection:

$$\text{Allowable minimum, mg } O_2/L = 1.41M - 0.0476M^2 - 1.11$$

Moderate level protection:

$$\text{Allowable minimum, mg } O_2/L = 1.08M - 0.0415M^2 - 0.202$$

Low level protection:

$$\text{Allowable minimum, mg } O_2/L = 0.674M - 0.0264M^2 - 0.577$$

Table 11.2. Examples of minimum dissolved oxygen concentration recommended for three different levels of protection of aquatic organisms.

Estimated natural seasonal minimum DO, mg/L	Allowable minimum seasonal DO, mg/L		
	High	Moderate	Low
14	9.3	6.8	4.9
12	8.9	6.8	4.8
10	8.2	6.5	4.6
9	7.7	6.2	4.5
8	7.1	5.8	4.3
7	6.4	5.3	4.0
6	5.6	4.8	4.0
5	4.7	4.2	4.0

For the oxygen concentrations, a small zone is to be allowed for dilution and mixing of the effluent into the receiving-water. Within that mixing zone, conditions may not meet the site-specific requirements. The Ministry recognizes such zones as a matter of policy and defines them on a case-by-case basis (MOE 1984). We have already suggested (Section 7.4.1) that the mixing zone be defined as a surface area, as recommended in the Hanna report to MISA (Hanna et al. 1987).

Column 5 deals with acute lethality of the whole effluent. This is defined by a lethal test with rainbow trout as specified by MOE (Craig et al. 1983). Some control orders for pulp mill specify that full strength effluent must not kill more than 50% of a sample of trout, i.e. the 4-day LC50 must be equal to or greater than 100% effluent. We recommend a standardization of the toxicity test, based on a fixed water use of 175 m^3 per

tonne of product, as described in section 7.5. The relationship to the federal toxicity test is outlined in Section 7.5.1. The toxicity criterion is the same for Levels III and IV, since there is no way of estimating an LC50 once it rises above 100% effluent, and therefore no way of specifying a further improvement.

Column 6 refers to sublethal toxicity as described in Section 7.4. For regulatory purposes the sublethal criterion should be based on whether or not deleterious effects are statistically significant in either of two laboratory tests: (a) a 7-day "larval survival and growth test" with fathead minnows; and (b) a 7-day life-cycle and reproduction test with Ceriodaphnia sp. Both tests are described by Horning and Weber (1985). The criterion applies to test-results at the dilution expected at the edge of a defined, site-specific mixing zone. Prior to regulatory action, any apparent sublethal effects should be confirmed by biological surveys of the aquatic communities in the receiving water (Section 7.4). However the laboratory tests should be taken as the absolute criterion of compliance and could be run on samples of water taken just outside the mixing zone.

Column 7 is concerned with total organochlorines, measured as "Total Organic Halogen" (TOX). These classes of compounds and their toxicity are discussed in Section 9. The rationale for reducing them need not be repeated here, but it is important to note that the technology for completely eliminating chlorine from the bleach plant has not been proven, assuming that we must produce white paper. The suggested levels of organochlorines are therefore compromises; they may be attained by a number of in-plant process changes, and to some extent by external waste treatment). Levels II, III and IV are all attainable by proven technology, as discussed below, but some mills would require extensive modifications to comply with the lower values. For mills producing bleached pulp, reduction of TOX will require some years to phase in new processes at appropriate times.

It might be mentioned that by our calculations, one Ontario bleached kraft mill has already attained Level II requirements for discharge of organochlorines, and two others are very close. None have attained level III, although the Red Rock mill which does almost no bleaching has, of course, an effluent that meets the Level IV value for TOX

11.3 Options for Achieving Goals

There are a number of approaches which mills can use to improve effluent quality to comply with the levels of achievement mentioned above. The technology is discussed elsewhere in the report, and the following is intended to summarise some of the major options available. Unless otherwise mentioned, all technology discussed below is proven on an industrial scale.

In the interests of simplicity, the following discussion addresses only those equipment and process modifications which have a significant effect on the effluent parameters in question. In most cases there are other potential measures which have marginally beneficial effects, and can be used effectively in combinations. Many have been mentioned in Sections 3 and 4 of this report.

The lists of options for achieving the goals are not intended to be exclusive, but simply to outline the most widely used possibilities, and serve as a basis for economic evaluations. In all cases a detailed engineering analysis of the mill process and site conditions is required to define the best way of complying with any regulations. There is little doubt that these engineering feasibility studies will uncover major difficulties of one kind or another in some mills, and that a satisfactory solution will tax the engineer's ingenuity. On the other hand, we have not allowed for the many possibilities for implementing minor improvements in addition to the major items discussed. Neither have we assumed that any new

technology would be used, whereas the current research activity suggests that there are better and more economical solutions around the corner.

11.3.1 Complying with Level of Achievement I

All mills in Ontario presently comply with Level I criteria.

11.3.2 Complying with Level of Achievement II

Any mill with conventional primary treatment system, whether a clarifier or sedimentation basins, can comply with the suspended solids limits mentioned of all levels of achievement, and all Ontario mills presently do so.

Compliance with the recommended BOD limits for level II and also for levels III and IV can generally be attained by any two of the following measures, presuming that the mill operation in general is in accordance with average modern operating practices, and has adequate systems to control spills of black liquor and unbleached stock:

Steam stripping the digester and evaporator condensates.

Replacing wet debarking with a dry system.

Exceptionally good brownstock washing

Oxygen delignification

Secondary treatment of the effluent.

If the receiving water provides little dilution, the DO limitation will always be the determining factor in defining the allowable BOD discharges. Some mills will require secondary treatment or oxygen delignification to attain the lower levels that may be necessary for small bodies of receiving water. In the most difficult cases, secondary treatment will be necessary.

To comply with the proposed limit on organochlorines mills will have to use either:

high substitution of chlorine dioxide for chlorine;

oxygen delignification; or

biological treatment.

In extreme cases two of the three measures may be required. Mills bleaching entirely softwood pulp will have the most difficulty, since they require the highest chlorine charges to attain market quality brightness.

We would expect mills which comply with this organochlorine limitation to also comply with the recommended lethality standard providing that black liquor losses are low and that wet debarking is not used (none of the mills which would be affected currently use wet debarking but some may have to improve brown stock washing).

11.3.3 Complying with Level of Achievement III

Compliance with BOD and DO requirements of level III will require the same installations as for level II, except that somewhat higher performance will be required for mills discharging to receiving waters of limited assimilative capacity.

To comply with level III limits for TOX, softwood mills can implement high chlorine dioxide substitution and oxygen delignification. However, in some cases one of the above-mentioned processes plus biological treatment will suffice, or they may elect to use some of the developing technology which is not yet fully proven. If a significant proportion of the mill furnish is hardwood, or the mill has a biological treatment system then either high substitution or oxygen delignification may suffice.

11.2.4 Complying with Level of Achievement IV

The BOD, toxicity, and dissolved oxygen objectives of level 4 can be attained with technology similar to that used in level III. The only difference is that mills on small watercourses are more likely to have to install biological treatment.

To comply with the recommended limit on discharge of TOX, softwood mills will probably require all three of the processes mentioned in 11.2..3 unless some of the new processes under development prove successful. Hardwood mills can probably comply by using any two of the three processes mentioned in 11.2.3.

11.3 Selection of Optimum Option

A simplified summary of alternative means of complying with the different levels of achievement is presented in Section 11.2 above. While these represent the principal possibilities available to the pulp industry, and served as the basis for much of the economic analysis in Section 12, the simplification of the presentation may mislead the reader who is not completely familiar with the industry into believing that selecting the best approach for any one mill is quite simple. This is not so.

As with most business decisions, selection of the most suitable technology to comply with whatever regulations or control orders are applied as a result of this report will be based on factors which can be predicted relatively accurately, such as the capital and operating costs associated with each alternative, and less predictable factors, such as long term regulations, technological developments and future customer demands.

If one assumes that the government, public pressure and technological developments will move toward complete elimination of chlorine and chlorine compounds from bleaching kraft pulp, then oxygen delignification clearly has a better long term future than increased chlorine dioxide substitution. The scope of our work has been restricted to proven technology, but we cannot ignore work such as that by liebergott et al (1987) which demonstrated possibilities of bleaching market kraft pulp, in the laboratory, without any chlorine. Schleinkofer (1983) has shown that an ozone stage following an oxygen delignification stage can further reduce chlorine requirements, hence reducing organochlorine discharges.

Future chemical and energy prices are quite unpredictable, but will have a major impact on the actual future costs of operating whatever processes are installed. If many mills elect to increase chlorine dioxide substitution levels substantially, one must wonder about the impact on the price of sodium chlorate, which is the predominant factor in the cost of chlorine dioxide. Clearly, if sodium chlorate prices drop, then chlorine dioxide substitution could become more economically attractive

In the final analysis, the **management of each mill must select the technology to be used**, since they are responsible for making it work and for its economic survival.

12. THE ECONOMICS OF IMPROVING EFFLUENT QUALITY

SUMMARY (1) There are four major compatible technologies which are capable of improving the effluent quality of bleached kraft mills. (2) Two of these technologies, high chlorine substitution and oxygen delignification, do not lead to any significant increases in production costs. For a number of mills, it is even profitable to use them to reduce the flow of pollutants. (3) The cost of securing major reductions in the emission of organochlorines will not have a significant impact on production costs. (4) Mills that have already committed resources to improving effluent quality will clearly find it less costly to meet the suggested effluent requirements than mills that have done little or nothing in the past to protect the environment. (5) The Ontario industry is not at a competitive disadvantage compared to the Swedish and U.S. in terms of tax treatments.

There are a large number of readily available alternative techniques representing proven technology which are capable of bringing about improvements in effluent quality. The cost of implementing environmentally beneficial changes in the production of sulphate pulp is very mill specific. Mills display a considerable lack of homogeneity in terms of production processes and the vintage of the capital equipment employed. Some mills in Ontario, for example, are very efficient in terms of both economic and environmental criteria; others, unfortunately, are not. The cost to a specific mill of meeting any common given medium or long-term environmental requirement is in part dependent on the existing technology employed by the mill and in part on the effort and investments that the mill has already made in improving the quality of the effluent. In consequence, mills that have paid little or no attention to improving effluent quality in the past will be faced with higher capital investment levels in meeting any new regulatory standard than will mills that have already made significant improvements in effluent quality.

With the above caveats firmly in mind, the objective in this portion of the report is to provide an estimate of the economic costs (and in some cases potential benefits) of improving effluent quality.

In other jurisdictions, the introduction of more stringent effluent quality regulations has been met initially with a large degree of hostility and in some cases hysteria from the industry. Typically, industry representatives have claimed that the more stringent regulations would at a minimum, destroy the competitive position of the industry and cause "billions of dollars...(to be)...poured into the mill sewers" (Gould 1980). It is interesting to note that the cost anticipated by the industry in meeting effluent guidelines promulgated under the US Clean Water Act of 1973 have been very much greater than the costs actually experienced. Arthur D. Little Inc., under a contract with the Council on Environmental Quality, estimated the cost for the US bleached kraft sector of meeting 1976 water quality standards as being equal to $7.70 in 1971 US dollars per tonne for operating costs in a mill of "efficient size"(equal in 1984 US dollars to $16.40 per tonne) and capital costs of $16,000 per daily tonne. The market price for US produced softwood bleached kraft was equal to $140 per tonne at the time of estimation. On the basis of these estimates it was concluded that a non-trivial number of mills would be forced to close as result of the effluent guidelines.(Arthur D. Little Inc. Staff 1972). Wrist (1973), reporting on two studies prepared for the National Council of the Paper Industry for Air and Stream Improvements Inc., indicates a similar range of values.

Data extracted from a preliminary study of the impact of the Clean Water Act on both the pulp and paper industry and on the environment indicate that the actual cost of meeting the regulations promulgated under the Act between 1973 and 1984 have been much less than those initially claimed by the industry (US EPA 1987). For most bleached kraft mills, the additional operating cost per tonne which result from

complying with EPA. effluent quality guidelines lies in the narrow range of $4 - $5.5 (expressed in 1984 US dollars) for mills which are similar in size and types of products produced to the nine Ontario kraft mills. This cost estimate is for both internal and external control measures. Many of the internal controls have already been adopted by Ontario mills. A number of mills are estimated to have costs below $4 per tonne-some as low as $2.59- and one mill as high as $6.87. It should be noted that a number of mills have had to meet effluent quality requirements that are significantly more stringent than those contained in the overall EPA guidelines. EPA estimates, which are based on engineering estimates generated from a set of model mill simulations, are generally considered to overstate the operating costs entailed by the Clean Water Act. We have chosen not to rely on the EPA estimates of the capital costs involved in complying with the effluent guidelines suggested in this report, primarily due to the fact that we have detailed data on mill specific capital costs and in addition that the suggested effluent quality standards are not the same as those currently mandated by the EPA.

There are four major technologies currently available which, if adopted, are capable of improving the quality of effluent from the kraft pulping process. Of the four technologies three can be classified as in-plant process changes: Oxygen delignification, high chlorine dioxide substitution and extended delignification. Oxygen delignification will lead to large reductions in the emission of TOX and to moderate reductions in BOD loads. High chlorine dioxide substitution is relatively efficient in reducing TOX levels but has little effect on the BOD level. Both processes are relatively easy to install in an existing mill. Extended delignification will normally lead to small reductions in both TOX and BOD. It is normally impractical to install extended delignification in an existing mill except when it is installed as part of a major rebuild and modernization programme. The fourth technology is biological treatment which is classified as external to the production process. Biological treatment is very efficient in removing BOD but is less efficient in removing TOX. Major problems with biological treatment are that it requires extensive land areas and it is expensive to install and operate. Table 12.1 provides a brief summary of the salient aspects of these four technologies.

Table 12.1 Simplified summary of effect on effluent quality of adopting some alternative technologies.

Process Modification	Reduction in BOD	Reduction in organochlorine	Reduction in fish lethality	Comments
Oxygen delignification	20 - 40%	up to 50%	Appreciable	Retrofit feasible
Chlorine dioxide substitution	None	up to 50%	Variable results	Retrofit feasible
Extended delignification	Modest	up to 20%	Little	Retrofit difficult
Biological treatment	Up to 90%	Up to 33%	Appreciable	Retrofit feasible but requires space

There are also a number of minor process changes, discussed in Section 3, which if implemented would lead to improvements in effluent quality. It should be also noted that the production of bleached

hardwood pulp requires substantially less chlorine than does the production of bleached softwood kraft and thus in consequence, the amount of organochlorines produced in mills using a hardwood fibre is substantially lower than for mills using softwood. The current trend toward pulping higher proportions of hardwood will inherently improve effluent quality.

Prior to assessing the economic impact on the Ontario industry of meeting the effluent quality goals given in Table 11.1, it is necessary to provide a general description of the costs and benefits of each of the four main technologies.

We have computed detailed estimates of the economic costs, and in same cases benefits, attached to each of the four major technologies on a mill-by-mill basis. These estimates take account of the currently installed systems, mill capacity and major local site constraints. After much thought, we have decided not to publish our detailed mill-specific data on the grounds that Ontario companies are in a competitive market and in consequence it might be inappropriate to provide company-specific data on important elements of operating costs. (Individual mills will be given access to data pertaining to their firm's specific costs). This creates a number of problems for us in the presentation of this section of the report. We could have provided, for example, detailed estimates for a "model" mill. We did in fact construct a "model" mill and generated detailed cost data for the introduction of all four technologies. This approach was rejected on the grounds that the variance across mills was very large and thus, due to the heterogeneity of mills, the "model" mill approach is of little value. Neither is it possible to present data in a "disguised" form since we believed it would be possible to identify specific mills. We have therefore chosen to present economic costs for mills at each end of the cost spectrum.

It should be pointed out that pulp producers are currently enjoying a highly favorable operating environment in terms of both production levels and market prices. Since the end of 1985, the list price for the benchmark northern bleached softwood kraft sold in US markets has increased from $390 US to $635 US (The latter price is equal to approximately $800 Can.) Canadian producers selling into European markets are currently receiving prices equal to $680 US per tonne ($850 Can.).

We have pointed out in Section 6.1 that real prices for market pulp have fluctuated considerably during he last 30 years. Thus the current relatively high prices being received by market kraft producers should not be thought of as being in any sense long run equilibrium prices. It would clearly be dangerous to attempt to predict the price of pulp over the next decade or more as this will depend significantly on the rate at which demand for pulp increases and on the amount of new capacity that enters the market, both in terms of kraft pulp and in terms of highly substitutable non-kraft grades. We have noted the recent range of prices simply in order to provide a background to the discussion on the costs involved in improving effluent.

12.1 Economic Cost of Secondary Treatment

SUMMARY. Although secondary treatment of kraft mill effluent is very efficient in reducing BOD, it is also relatively expensive. We estimate that operating costs will be in the range of $2-2.5 per tonne of bleached kraft. Capital costs are site specific, but for a mill producing 750 tonnes per day are unlikely to be below $15 million.

It has been shown in Section 6.4 that whereas secondary treatment is standard practice in US mills and is becoming increasingly common standard in Sweden and Finland, only 3 of the 9 sulphate mills located in Ontario have biological treatment facilities. In general, companies do not believe that the cost of installing and operating a secondary treatment facility is warranted in relation to the environmental benefits that secondary treatment typically yields.

Biological treatment of effluent from kraft mills has proven to be a very effective method of reducing the discharge of traditional pollutants. The most common means of providing biological treatment is by the installation of an aerated lagoon. A properly sized and operated aerated lagoon is very efficient in reducing BOD levels and in significantly reducing the acute lethality of the mill effluent to fish. A typical aerated lagoon will reduce BOD levels by between 60-90% and in addition will sometimes virtually eliminate the acute lethality of the effluent to fish.

The major alternative to aerated lagoons for providing secondary treatment is the activated sludge method. Activated sludge systems are very efficient in reducing BOD levels and rendering the effluent non-acutely lethal to fish. Reductions in BOD levels are typically in the range of 80-95%. Activated sludge systems are also more efficient in removing organochlorine than are aerated lagoons, although one must question the final destination of the organochlorines. Reductions of 30-50% in organochlorine levels have been reported in Finland. However, it should be pointed out that there has not been a significant amount of research directed at ascertaining the efficiency of activated sludge systems in reducing organochlorine. Major problems associated with activated sludge systems are sensitivity to shock loads and the large volume of sludge that has to be dewatered and disposed of (Committee for the Gulf of Bothnia 1987).

The capital cost of constructing an aerated lagoon treatment facility will vary considerably across mills. For a mill producing around a 1000 tonnes a day of kraft pulp and using an average amount of water, capital costs will range between a low of $15 million and a high of $25 million. The latter figure would only apply in a case where the mill faced very difficult and extensive site problems. The most reasonable estimate for the capital cost of installing an aerated lagoon for the size of the mill given above is $20 million (1988 dollars). Our analysis indicates that the capital cost of and aerated lagoon, per tonne pulp produced, decreases slightly as the size of the mill increases. Operating costs, including electrical power, maintenance, labour and nutrients, will be equal to $2.5 per finished tonne of pulp.

Activated sludge systems are more expensive to construct and operate than are aerated lagoons. Based on European and US experience with activated sludge systems, capital costs are estimated to be 30% higher than those prevailing for aerated lagoons. Operating costs per tonne of finished product are likely to be in the range of $4-5.

Although the above costs are clearly not insignificant and will undoubtedly lead to a small reduction in the profitability of mills required to provide secondary treatment, it should be noted that all mills in the US and some bleached kraft mills in Finland and Sweden have already installed secondary treatment facilities. (In

Sweden, the biological treatment of effluent is likely to be adopted by all mills in the near future as a result of the very stringent effluent quality requirements that are being introduced. This is discussed in Section 4.4.8).

12.2 Cost and Benefits of Installing Oxygen Delignification

SUMMARY.The introduction of an oxygen delignification stage in an existing bleached kraft mill will lead to a lowering of variable costs. Given that prices for major chemicals used in the bleach plant are higher in Ontario than in most other producing regions, the savings to be obtained from oxygen delignification are estimated to larger for Ontario mills than for mills in other jurisdictions. For most mills, oxygen delignification represents an economically attractive means of improving effluent quality and reducing operating costs.

It is widely accepted that oxygen delignification (occasionally known as "pre-bleaching") is capable of providing a large increase in the quality of effluent flowing from a sulphate mill compared with a traditional "benchmark" sequence . Oxygen delignification is a proven process as shown in Section 3.3 of this report. The number of systems installed has increased fairly rapidly in the 1980's. (Figure 3.10)

The reduction in the discharge of pollutants from sulphate mills using an oxygen delignification stage is well documented, and is discussed in Section 3.3.12-17. Generally, BOD, COD, colour and organochlorine discharged from the bleach plant will drop by about 50% when an oxygen delignification stage is introduced.[1]

It is widely agreed that the introduction of an oxygen stage permits a significant reduction in chemical costs per tonne of finished product. Savings in chemical costs per tonne of finished product will vary across mills depending upon mill location, existing chemical consumption and costs and on the type of oxygen delignification system installed. For an Ontario mill currently on the high end of the chemical consumption spectrum, net savings in chemical costs are estimated to be of the order of $14-15 per tonne of softwood pulp. (These savings are net of the variable cost of producing oxygen and are based on chemical costs prevailing f.o.b the mill in late 1987. It is assumed that pulp is being bleached to 90 Elrepho brightness). The net saving in variable costs that can be attributed to the introduction of oxygen delignification will be $11-12 per tonne for softwood pulp in mills on the high end of chemical consumption. (The major reasons for the savings in variable costs not equalling the savings in chemical costs are that we have allowed for increases in the power requirements, increased maintenance costs and for a small reduction in yield). For mills at the low end of the chemical consumption spectrum, the net savings in chemical costs are around $10 per tonne of softwood pulp. In this case the savings in variable costs are equal to $7 per tonne.

It has been suggested by at least one company that our estimates of the variable cost savings due to the installation of an oxygen delignification stage should be reduced to allow for the fact that the introduction of oxygen delignification will require the use of a portion of any "spare" boiler capacity that could otherwise have been used for a future possible marginal increase in pulp production. We believe it would be inappropriate to include such costs on the grounds that they are very highly speculative in nature. Our

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1 Note that other mill processes generate BOD and COD, so improvement of these characteristics of the mill effluent will be less than 50%.

estimates of the mill specific cost of complying with the alternative levels of effluent quality are firmly bases on existing operations in the mills.

It is interesting to note that the benefits of oxygen delignification are likely to be higher in Ontario than in most other regions. The major reason for this is that the price of chemicals f.o.b the mill is on average much higher in Ontario than is the case for British Columbia, Sweden and many parts of the US This is the prime reason why the cost savings reported above for high end chemical users are above those contained in recent articles on the economics of oxygen delignification. (Harper and Tench 1987, Arhippainen and Malinen 1987).

In the case of hardwood bleach lines, the economic and environmental benefits of installing an oxygen delignification stage are somewhat lower than those estimated for the softwood situation. With respect to the environmental benefits, the introduction of an oxygen bleaching stage will reduce the discharge of organochlorine by approximately the same percentage as it does in the softwood case. Given that the absolute reduction in chlorine usage will be lower (simply because the amount of chlorine required to bleach hardwoods to a given brightness level in the traditional non-oxygen sequences is less than it is for softwoods) it follows that the absolute cut in organochlorine emissions will be lower. Due to the fact that the absolute reduction in chemical requirements will be lower in the case of hardwood kraft processes, savings in variable costs will not approach those cited for softwood kraft processes.

The capital costs for installing a medium consistency oxygen delignification stage in an existing mill in Ontario will be approximately $15 million (1987 dollars) for a 750 tonne-a-day mill. This estimate is based on published data in trade journals, discussions with equipment suppliers and mill engineers. In addition, we have had access to cost feasibility studies undertaken by a number of mills. The cost of installing the process in higher volume lines would increase the total, but not the average, capital costs. Additional capital costs could be incurred for modifications to the recausticising process, modifications to the recovery system to make up any shortfall in capacity, and for improvements in the brownstock washing system. These factors could increase the capital investment required by $2-$5 million, especially in situations where existing installations are at best marginal. Where these additional costs are high, there would also be some other benefits due to the modernization of obsolete equipment.

The economic efficiency of oxygen delignification has been widely discussed in industry trade journals and equally widely misunderstood. (Galloway, Schmid and Lebidoff 1987, Idner 1987, Tench and Harper 1987, Arhippainen and Malinen 1987.). In order to provide an estimate of the economic costs and benefits of introducing oxygen delignification we assume an annual flow of savings in variable costs equal to $2 million dollars for a mill with a capacity of 750 tonnes a day. Capital costs are assumed to be equal to $15 million (1987) dollars and the process is assumed to have a physical life of 15 years. We have chosen capital cost estimates that are at the top-end of the range and variable cost savings that are in the middle of the range. Given the above assumptions the internal rate of return (IROR) on a before-tax basis equals 11%. In our mill by mill analysis, the pre-tax IROR ranged between a low of 8% and a high of 15%. Thus even if we ignore the implications of improved effluent quality, oxygen delignification by itself is an acceptable investment for a number of mills when judged against hurdle capital costs. With respect to the latter, these appear to be in the range of 12-14% on a before-tax basis for leveraged equity investments and around 7-9% on an after-tax basis. (Jenkins 1977, Tarasovsky, Roseman and Waslander 1980, Anderson and Bonsor 1985). The introduction of the existing Canada-Ontario corporate tax regime into the model confirms that after-tax IROR'S are above the hurdle costs of capital for a wide range of assumptions on the tax position of the firm.8%15

The technology of oxygen delignification is discussed in Section 3.3. Technical solutions to the various potential difficulties that oxygen delignification retrofits can cause are described, including recovery boiler overload, and the effect on the chemical balance between caustic and chlorine in the Canadian market.

One additional advantage of oxygen delignification that needs to be mentioned is that it reduces the cost of any subsequent treatment in a secondary treatment facility, mainly because of the reduced flows that the oxygen stage permits.

12.2.1 Quality Considerations Related to Oxygen Delignification

SUMMARY. Oxygen bleached kraft pulp is estimated to represent 16-19% of world market pulp capacity by 1989. Mills are not experiencing any difficulty in marketing the product, although management of some Ontario mills have expressed concerns about losing some of their customers if they install oxygen delignification. A number of mills are experiencing customer preference for an oxygen bleached pulp on environmental grounds.

We estimate that by 1989, between 16-19% of world market kraft capacity will be accounted for by mills using an oxygen delignification stage (Fig. 3.10). The interest in the oxygen process in North America has increased dramatically in the last six months. We are aware of a number of detailed feasibility studies being conducted by mills in Canada and the US. Part of the reason for this interest is due to mills anticipating regulatory action on controlling organochlorine discharges.

A number of producers of market kraft indicated that major buyers were expressing a preference for oxygen bleached pulp on environmental grounds. This, no doubt, is related to the considerable publicity generated by the Dioxin issue in some cases, and also to the high probability of German authorities regulating the organochlorine content of imported pulps.

A number of senior company officials in Ontario have stated flatly that Oxygen bleached pulp cannot be sold on the market because it is of lower quality to pulp produced in the traditional manner. In particular, they opined that because viscosity is lower in the oxygen bleached pulp, buyers would always have a preference for non-oxygen bleached pulp on the grounds that the latter pulp is stronger. As we have shown in Section 3.3.15, this is erroneous.

The number of companies shown in Table 3.6 which have purchased additional oxygen delignification systems after gaining full scale operating experience with their first ones lends credibility to claims that oxygen delignified pulp can be sold profitably.

We asked a number of major sellers of both oxygen and traditional bleached pulp whether or not they experienced difficulty, or anticipated any difficulty, in selling an oxygen bleached pulp. Most agreed that viscosity was a " Red Herring", both technically and in terms of buyer preference. One executive from a non-Ontario mill stated that a major reason for his mill planning to introduce an oxygen stage was buyer preference for an oxygen bleached product.

12.3 Costs and Benefits of Extended Delignification

SUMMARY. Extended delignification yields moderate reductions in both BOD and organochlorine emissions. Owing to the difficulties involved in retrofitting an existing mill with the system, this option can only be considered when a new mill is being constructed or a mill is being extensively rebuilt. In these cases, extended delignification represents a viable method for achieving small improvements in effluent quality.

In this part of the study we consider the costs and benefits of introducing extended delignification. This basically involves extending the cooking time in the digester. From an environmental view-point, extending the cook and thus driving the Kappa number down is beneficial. By itself, extended delignification will not yield a very significant improvement in the quality of mill effluent. Based on Swedish experience in operating an extended cook and on mill models, the process leads to only very marginal reductions in BOD. (Arhippainen and Malinen 1987). Reductions in Organochlorine and colour were more significant, but very much lower than those achieved by oxygen delignification. Whereas oxygen delignification reduces organochlorine and effluent colour by around 50%, extended delignification would probably achieve improvements of under 25%.

Much of the recent interest surrounding the extended delignification process has been in the context of using an extended cook in conjunction with an oxygen delignification stage. Extended cooking and oxygen delignification together would yield a large improvement in effluent quality. For softwood pulp lines, TOCL levels have been calculated to be around the 2.5 kg per tonne of output. Reductions in BOD and colour are also improved- although of small magnitude compared with the "straight" oxygen sequence.(Committee for the Gulf of Bothnia 1987).

Extended delignification (down to a Kappa number of around 25 in a "stand-alone process" or to around 14 in conjunction with oxygen delignification) yields a small reduction in chemical costs. In a "stand-alone" case, the cost saving per tonne of softwood pulp is unlikely to be greater than $3. When coupled with an oxygen delignification stage, the marginal saving in chemical costs is even smaller. The flow of economic benefits from extended cooking is thus smaller in absolute terms than from the introduction of oxygen delignification. We estimate the savings in chemical costs to of the order of $900,000 per annum for a 750 tonne a day softwood line in the "stand-alone" case and $500,000 when used in conjunction with the oxygen stage.

The capital cost of introducing extended cooking will be highly variable across mills. For a new mill the cost of introducing an extended cook will be very low. Introducing this process into an existing mill can be relatively costly, especially if extensive rebuilding of the line is required, and in many cases would be completely impractical because of space limitations. However, the combination of oxygen delignification and extended cooking-given the very large environmental benefits-may well provide a more economically efficient method of reducing or improving effluent quality than stand-alone secondary treatment.

12.4 High Chlorine Dioxide Substitution

SUMMARY. High chlorine dioxide substitution represents, for most mills, an attractive means of reducing the discharge of organochlorines.

For all kraft mills in the province, the substitution of chlorine with chlorine dioxide represents a relatively low cost method of reducing the discharge of organochlorines. The increased use of chlorine dioxide has no effect on BOD levels and its impact on acute lethality is at best uncertain. (Section 3.3.10)

With respect to operating costs, Figures 3.5 and 3.7 show that overall chemical costs are relatively unaffected up to substitution levels of 50%. Even substitution of up to 70% of chlorine with chlorine dioxide entails only relatively minor changes in chemical costs for the typical Ontario mill operating with 5% to 15% substitution.

Note that the lowest bleach chemical cost is achieved in the 35% to 50% substitution range.A mill currently operating in this range would experience an increase in chemical costs of about $2.50/t pulp if substitution increases to 70%.

The major cost of increasing the use of chlorine dioxide is the capital cost of increasing generator capacity. We have obtained detailed cost estimates for facilities of various different sizes. For Ontario mills, the capital costs would range between a high of $5 million and a low of zero. The latter is for a mill that has adequate surplus capacity. Given a life length of 12 years for the chlorine dioxide generation, the cost increase per tonne of pulp is very small.

12.5 Cost of Meeting Specific Effluent Quality Guidelines

SUMMARY The cost of complying with the suggested organochlorine requirements of levels II and III will not impose significant cost penalties on firms. A number of firms would be required to remedy site specific dissolved oxygen problems. In general, dealing with site specific problems is more costly than reducing the discharge of organochlorines.

In this section of the study the aim is to provide an estimate of the costs that would be faced by the industry if the Province adopted various specific effluent quality requirements. It should be noted that since existing mills are not homogeneous in terms of size, vintage of major parts of the capital stock or the production sequences employed, actual costs will vary across mills.

Table 11.1 provides a summary of four "Levels of Achievement" for effluent quality. Our first aim in this section is to provide an estimate of the compliance costs that would be borne by mills in meeting each of these levels.

A small proportion of the total production of kraft pulp in Ontario takes place in non-integrated mills which are below the minimum economically efficient scale. In the absence of site specific advantages, such as lower than average fibre costs, mills of less than minimum efficient scale are at a cost disadvantage compared to larger mills. This is readily apparent in our estimation of the mill specific costs of complying with the suggested effluent quality guidelines, especially where secondary treatment facilities are required. Non-integrated mills below minimum efficient scale have compliance costs (per tonne product) which

exceed those of mills of efficient scale. The costs of many aspects of mill operation which are unrelated to environmental protection will also be relatively high in the very small mill.

In the long run, non-integrated mills which are below minimum efficient scale will be less than competitive and, if not expanded or converted to another product will leave the industry .

The problem of economic scale is modified or eliminated if the production of kraft pulp occurs in an integrated environment. This is primarily due to the economies of scope, which can be non-technically defined as savings which result from the presence of joint costs in the production process.

12.5.1 Level of Achievement II

The majority of mills in the Province have an effluent quality that is significantly inferior to that suggested by our Level II requirements. The cost of complying with Level II requirements varies widely across mills. As we have noted above, detailed estimates have been compiled for the costs faced by each mill in complying with effluent requirements suggested by levels II-IV. Owing to the difficulty of effectively coding mill specific data, we are reporting our results in a generic as opposed to a specific manner. We present results for mills that are at each end of the spectrum in terms of compliance costs together with the costs faced by the "median" mill.

One mill already meets all of the effluent quality standards suggested by level II. In the case of one other mill, all that is required for compliance is the construction of an outfall diffuser at an estimated capital cost of $15 per annual tonne of production.

The costs faced by mills in complying with the suggested emission requirements for organochlorines are, with one exception, relatively small. For a number of mills, the optimal economic strategy is to install an oxygen delignification stage. For the four mills for which we estimate oxygen delignification to be the least cost method of complying with the organochlorine discharge limits, the internal rate of return (IROR) ranges between a high of 15% to a low of 8%. For three mill, oxygen delignification can be justified on purely private grounds since the IROR is above the hurdle cost of capital.

A number of mills are faced with the problem of complying with water quality standards for dissolved oxygen in local receiving waters. The cost of remedying the "local" or traditional" water quality problems are typically more expensive that the cost of complying with the limitations on the emission of organochlorines. The cost of complying with all level II requirements for mills that must remedy local receiving water problems will necessitate capital investments ranging from $15-$173 per tonne. In order to report capital costs on a uniform basis, we have divided the estimated total capital cost by the annual production rate. The resulting capital investment requirement per tonne must not be interpreted as being equal to the average fixed cost that must be borne by a mill in meeting the effluent quality requirements. The latter are of course much lower than the former. For example, if we assume a real cost of capital equal to 10% and a 20 year for the capital asset, the estimated average fixed cost per tonne of pulp for complying with the level II dissolved oxygen requirements range between a low of $3 and a high of $25. It must be noted that these estimates are prior to the introduction of tax considerations. Given that most capital investments are accorded favorable depreciation provisions, the real costs to the firms will be lower that those suggested above.

Table 12.2 presents summary data for the costs of achieving level II requirements for the "high", "median" and "low" mills in terms of compliance costs. In all cases the average costs are close the medians shown here.

Table 12.2 Costs of achieving level II, ranked by IROR, excluding mills with zero cost.

	Capital Investment cost. $/daily tonne	Change in operating cost $/tonne	IROR %
Low	$173	+$2.4	null
Median	$56	-$7.7	+11%
High	$64	-$11	+15%

It is worth mentioning that the 'high' a cost case is very exceptional. The mill is very small and is of very dated vintage in terms of major items of capital equipment. Given that the mill is far below the size required for optimal performance as a kraft mill, it is not surprising that unit production costs will increase at a very much higher rate than is the case for any other mill in the province.

12.5.2 Level of Achievement III

For almost all mills, the incremental costs of moving from level II to level III is very small. Given that the problems faced by mills with dissolved oxygen deficiencies have been remedied in the level II stage, the reductions in organochlorine emissions in the level III stage do not entail any significant changes in production costs.

Mills can meet the level III requirements by the introduction of oxygen delignification or, where an oxygen stage was installed to meet level II requirements, high chlorine dioxide substitution.

Table 12.3 Costs of achieving level III, ranked by IROR, excluding mills with zero cost.

	Capital Investment cost. $/daily tonne	Change in operating cost $/tonne	IROR %
Low	$191	+$2.4	null
Median	$82	-$7.3	+ 4%
High	$63	-$8.7	+11%

It is readily apparent that the major improvements to effluent quality which are implied by the move from level II to level III can in most cases be accomplished without major costs penalties. The major reason for

this is that the required reduction in organochlorine discharges can be achieved by internal process changes and do not require the installation of an external treatment facility.

12.5.3 Level of Achievement IV

The effluent quality standards suggested by level IV represent what we believe to be the best achievable by softwood mills with existing proven technology. They are in fact very comparable to the effluent quality requirements being mandated by the Swedish authorities and which must be met by a number of Swedish mills by 1991.

In order to meet level IV requirements, all bleach kraft mill would need to be using high chlorine dioxide substitution, oxygen delignification and have a biological treatment system. In addition, non-trivial changes such a improving the brownstock washing system and eliminating hypochlorite bleaching stages would be required.

For two mills, the cost of complying with level IV requirements is very small. In one case the reason is that the mill is bleaching only a very small percentage of total pulp output. In the other, the firm has already invested an impressive amount of money in securing improvements in effluent and production quality.

Table 12.4 provides summary data for the costs of moving from level I to level IV. The two mills that face very small costs in achieving level IV have been excluded from the table.

Table 12.4 Costs of achieving level IV, ranked by IROR, excluding mills with zero cost.

	Capital Investment cost. $/daily tonne	Change in operating cost $/tonne	IROR %
Low	$191	+$2.4	null
Median	$144	-$8.7	-1%
High	$89	-$11	+9%

For mills without pre-existing secondary treatment, the major cost element in moving from level III to level IV, is for the installation of such systems.

Although it is technically feasible for all mills to achieve level IV effluent requirements by using existing production technologies, even for those using a 100% softwood furnish, it is less than clear that mills should be asked to move to this level immediately. Given the large amount of research that is being conducted into non-chlorine and low chlorine bleaching it is possible that less costly and more environmentally effective technologies may become available in the near future to enable firms to move efficiently from level III to level IV. We believe that it may be prudent to wait about 5 years before considering whether or not to require mills in the province to meet the stringent water quality requirements envisaged by level IV.

12.5.4 Comments on Compliance Costs

It is apparent from our detailed analysis that estimated compliance costs vary considerably across mills. For bleached kraft mills that are operating at, or close to, minimum efficient scale, the cost of moving from level I effluent quality to level III quality would not imply a serious penalty in terms of the required increase in the average cost of production. For these mills, the real cost of achieving level III effluent quality is small, The estimated IROR for this group of mills ranges from a high of 11% to a low of 3%. (For one mill, the required capital investment is in fact zero and operating costs are not estimated in increase when effluent quality is improved to the level III standard). In general, mills that have already committed funds to improving effluent quality face lower costs in meeting level III guidelines than to mills that have committed few resources to improving effluent quality. In the case of two smaller mills, the real costs of moving from the existing level of effluent quality to the level III standard are very small. In these two cases we estimate the IROR to be between 11% and 7%.

The above mills operating near to or above minimum scale are responsible for close to 90% of the production of bleached kraft pulp in the province. One mill of very sub-optimal scale faces very high costs in securing any significant improvement in the quality of its effluent. As we noted in our discussion of the costs of attaining level II requirements, this particular mill has a fairly dated vintage for major items of capital equipment. The mill currently have very high values for BOD and TOX discharges per tonne of pulp. We comment on this particular case in Section 12.6.7.

It is interesting to note the compliance cost that have been estimated for US mills in meeting the EPA regulations on water effluent standards in force in 1984. Based on set of "model" mill equations, the median mill in the US faced an estimated capital investment cost equal to $117 Canadian (1987 dollars) per tonne of pulp production together with an increase in the average variable cost of producing a tonne of pulp equal to $7 Canadian (1987 dollars). The median Ontario mill is estimated to be able to meet the level III requirements with a capital investment cost of $82 per tonne of output and a decline in the average variable cost of production of $7.3. (We have deliberately excluded those Ontario mills that already have secondary treatment from this comparison with the US.) Very small US mills (300-350 ADt/day) faced compliance costs that were estimated to be much higher than those faced by the median mill. Capital investment cost for a small US mills were equal to $160 Canadian (1987 dollars) per tonne and the increase in the variable cost of production to $8 Canadian. (1987 dollars) per tonne remarkably close to that estimated for the compliance cost to moving to level III for a small Ontario mill. We are not suggesting that the estimated US compliance cost should serve in any way as a bench mark for the Ontario industry. Indeed, we have noted in Section 12.1 that the results from the "model" mill estimating technique may well lead to an overestimate of actual costs that are incurred by the US mills. It should also be noted that the US estimates were based on 1984 compliance costs and since that time many US mills have been faced with additional effluent quality requirements in term of complying with acute lethality regulations (Section 6.4.2) .

Given the above caveats, the comparison does however serve to put our cost estimates in perspective. The major reason for the lower cost estimated for Ontario mills in meeting the level III guidelines compared with those estimated for US mills in complying with EPA requirements in the recognition accorded to the importance of inplant process changes in meeting the level III guidelines.

The major costs entailed by the move from level III to level IV fall on those mills that would have to install biological treatment facilities in order to meet the effluent quality standards suggested by level IV.

12.6 Economic Impact on Mills

SUMMARY Although the Pulp and Paper industry in Canada has frequently claimed that it is at a significant disadvantage compared with Swedish and U.S producers in terms of tax and/or subsidy treatments, we show that Ontario producers have in fact been treated very advantageously in both these aspects of government policy. The suggested effluent quality guidelines will not cause a financial hardship for Ontario mills nor lead to mills exiting the industry.

Pulp and paper companies have been less than enthusiastic in committing resources to projects that would produce large environmental improvements. Although it is of course logical for firms to resist attempts to regulate a reduction in the amount of pollutants emitted from the kraft pulping process on the grounds that such regulations will increase the average cost of production, the specific objections advanced by industry are less than convincing. The objections typically raised in response to requests by government for the industry to spend monies on improving effluent quality have been to the effect that the industry is not financially able to do so or that all available funds should be spent on improving factor productivity as domestic producers must compete in a very competitive world market. When it is pointed out that all producers in the US and most producers in Sweden have spent considerably more on securing environmental improvements than have Canadian domestic producers, and in addition that it is highly probable that producers located in major production regions outside Canada can be expected to face increased costs from complying with tightened effluent quality regulations in the future, the general response has been that US producers face a more favorable corporate tax environment than do Canadian producers and in consequence are able to spend more monies on improving effluent quality. In the Swedish case, the Canadian industry holds the view that not only is the tax treatment of Swedish producers more favorable than that faced by domestic producers but that in addition the Swedish industry is heavily subsidized. Thus, it is argued, domestic producers should not be required to meet tightened effluent quality guidelines simply because this would place them at an "unfair" disadvantage compared with subsidized (either directly so or via less obvious preferential tax treatments) foreign companies. We now show that the economic and financial arguments advanced against tightening effluent quality standards are at best misleading.

12.6.1 Corporate Tax Environments

The Canadian pulp and paper industry has frequently claimed that producers located in other major producing regions, particularly those in the US and Sweden, face a more favorable tax environment than do Canadian producers (CPPA, Canada 1978). Although this claim may have been accurate for tax environments in the late 1960's and early 1970's, the Canadian tax changes of 1972, 1975 and 1978 significantly liberalised tax treatments for the industry (Canada 1979, Anderson and Bonsor 1985). In particular, the introduction of very fast depreciation allowances for machinery and equipment (accorded a two-year life) in 1972 created a very favorable tax environment for new capital investments in the industry. This favorable environment was enhanced by the presence of investment tax credits (ITC'S) first introduced in 1975.

It is important to realize that there is a very significant difference between statutory and effective corporate tax rates. The imposition of a tax on corporate income will cause the effective after tax internal rate of return (IROR) to diverge from the before-tax IROR. In the absence of inflation, the statutory (or nominal)tax rate will only be equal to the effective tax rate when front end abatements are absent. The

effective tax rate will be identical to the statutory rate when depreciation for tax purposes equals economic depreciation (where the latter is defined as the marginal change in the market value of the asset) and where there is no investment tax credit (ITC). If inflation is present, depreciation allowances for tax purposes must be indexed in order for the two to be equal.

Recognition of the fact that the after tax rate of return on capital assets is not simply a function of the rate at which corporate income is taxed has led governments to introduce a large number of changes to the corporate tax environment aimed at increasing the incentive to invest by decreasing the marginal effective tax rate (METR). The METR is defined as:

$$(r-s)/r.$$

where r is the pretax rate of return and s the after tax rate of return.

In both Canada and the US there have been two distinct classes of widely used investment incentives: those that affect the size of the tax wedge by increasing the present value of depreciation allowances and those that affect the after-tax IROR by granting incentives over and above the alteration of the timing of the depreciation stream. In Sweden, tax incentives have been both "front end" and "back end" in nature, taking the form of accelerated depreciation allowances and the opportunity to "shelter" a portion of profits from tax by placing income in investment reserve funds.

The most rapid method of accelerating depreciation allowances is to permit expensing. In this case,the entire cost of the asset is written off against income in the year of acquisition. Under expensing the METR would be equal to zero.

In Canada and the U.S., Investment incentives not related to the timing of depreciation allowances have taken on two main forms: the investment allowance method and the tax credit method. The former allows the firm to write off a given percentage of the asset immediately and then apply normal depreciation. With the latter, the firm is allowed a tax credit equal to a given percentage plus depreciation either on the entire amount or on the amount remaining after the asset has been reduced by the ITC.

Any change in the ITC or the manner in which depreciation for tax purposes is calculated will lead to changes in METR's and after-tax rates of return.

In Sweden, although there are provisions for accelerated depreciation allowances, the major incentives take the form of allowing -in some instances compelling- firms to "shelter" a percentage of profits from tax by the creation of tax free reserve funds. Throughout the course of this study, Canadian industry and government officials have constantly asserted that the tax treatment of the Swedish industry is much more beneficial than that accorded the Canadian industry. Given that this view is widely accepted (almost to the point that it is a tenet of faith), we feel it would be helpful to provide a brief description of the major provisions of the Swedish corporate tax system.

12.6.2 Swedish Corporate Tax Environment

The Swedish corporate tax system is fundamentally different to North American tax systems in both concept and application. The Swedish system is typified by a very high nominal tax rate currently 52%, a reduction from the even higher levels in force through the 1970's and early 1980's, and a large number of "special" provisions dealing with voluntary and involuntary reserves. In addition to the high nominal tax

rate, companies are also liable for a profit "sharing Tax". The profit sharing tax, introduced in 1984, is levied on a base which is computed as being the after tax income of the firm plus sums deposited in reserve funds. The resulting nominal profit level is adjusted for inflation and reduced by 6% of cash salaries. The tax rate is equal to 20% and the profit sharing tax is deductible in the tax assessment in the following year. The effective rate for the profit sharing tax is difficult to calculate due to the inflation adjustment on the value of assets and liabilities. We estimate that the maximum effective rate for the profit sharing tax will be 5%. For many Swedish pulp and paper companies the effect of the profit sharing tax will be limited to 2-3%.

It is clear from the above that the statutory or nominal tax rate combined with the profit sharing tax faced by Swedish companies is much higher than that faced by Canadian companies. Swedish firms face a nominal rate that is around the 54-55% level. The combined Canada- Ontario nominal rate for the 1988 tax year will be 44.34%. (We are assuming here that Ontario does not reduce the provincial rate in response to the broadening of the income base caused by the 1988 tax reform).

Whereas in most corporate tax systems firms are accorded "up-front" tax advantages in the form of accelerated depreciation and other investment incentives, the major advantages available to Swedish firms are "back-end" rather than "front-end" in nature. Both the "front-end" and "back-end" advantages serve to create a wedge between the nominal and the effective tax rate.

Depreciation

The major up-front tax advantage accorded Swedish firms is that pertaining to the acceleration of depreciation charges. In may respects, the depreciation provisions are similar to those available to firms domiciled in Canada. With respect to machinery and equipment, assets with a useful life of 3 years or less are expensed. All other machinery and equipment is subject to two rules: a main "30" rule and a supplementary "20" rule. The main rule allows depreciation on a 30% declining balance basis. The supplementary rule permits firms to opt for a 20% straight line depreciation on the initial procurement cost of the asset. Each year, the firm has the right of election in choosing the "30' or "20" rule. For example, the purchase of machinery and equipment for $100 yields the following depreciation charges:

	30 RULE	20 RULE
Year 1	$30.00	$20.00
Year 2	$21.00	$20.00
Year 3	$14.70	$20.00
Year 4	$10.89	$20.00
Year 5	$7.62	$20.00

The optimal path for the firm is to use the "30" rule for years 1 and 2 and then switch to the "20" rule in year 3. However, since depreciation is applied to the total machinery and equipment pool, a company that is adding significant amounts of new capital will not find it beneficial to switch to the "20" rule. Cooke (1988) contains a detailed analysis of financial reporting and accounting conventions for Sweden).

With respect to investment in buildings, depreciation is taken on a straight-line basis. In manufacturing sectors, buildings are allowed a 4% straight-line basis, with 6% being allowed during the first 5 years. (In the chemical and cellulose sectors, the 4% rate is increased to 5%.)

On balance, the Swedish provisions for accelerated depreciation in the manufacturing sectors are considerably less generous than the existing method allowed Canadian producers. The existing (1987) rules allow Class 29 assets to be written-off in 3 years (25-50-25). The Canadian tax reform of 1988 will, by 1991, replace the 25-50-25 rule with a 25% declining balance method (subject to an "available for use" rule and a half-year convention). Clearly, the proposed Canadian rules on depreciation are less generous than the existing Swedish rules. However, the Canadian nominal tax rate will decline significantly as a result of the tax reform, and thus income will be taxed at a much lower rate in Canada than in Sweden.

Investment Reserves.

A unique feature of the Swedish approach to the taxing of corporate income is the presence of voluntary and involuntary profit regulating measures. Most of these measures allow manufacturing companies to temporarily postpone paying corporate taxes. The existing system is comprised of the following provisions:

General Investment Reserve

All Swedish companies may allocate up to 50% of pre-tax profits to a reserve against future investments. Sums allocated to the reserve are deductible from taxable income. Seventy five percent of sums allocated to the reserve are held in a non-interest bearing deposit in the Bank of Sweden. Although payments into the reserve are, subject to the 50% rule, at the discretion of the corporation, government permission is required when the company wishes to use the monies in the reserve. Provided that reserve funds are used to purchase machinery, equipment, buildings, research and development, education of employees or for the marketing of Swedish products in export markets, permission is normally granted. When reserve funds are used with official approval no tax liability is created. However, only the cost of an asset net of the amount supplied from the reserve fund will qualify for depreciation. If funds are withdrawn without approval, the amount plus a 20% gross-up penalty becomes taxable. After a 5 year period from the time funds are deposited in the reserve, a company can automatically withdraw 30% of the initial deposit without approval or penalty provided the monies are used for either the construction (or maintenance) of buildings or for the purchase of new machinery and equipment.

The real value of the general investment reserve fund in reducing a company's effective tax rate is not as large as appears on the surface. In particular, firms using funds from the reserve for the purchase of capital assets do not receive any benefit in the form of depreciation allowances since such assets are considered to be fully written off for tax purposes. In the limit, the investment reserve provides a useful alternative to paying tax at the statutory rate of 52% on 50% of profits. Even if such funds are never withdrawn, firms are better of putting 50% of pre-tax profits in the reserve (implying a nominal tax rate of 50%) than the alternative of paying the tax to the government at the statutory rate of 52%. In the more reasonable case where the funds are withdrawn, the implicit cost to the firm of using the investment reserve to shelter profits is the interest cost forgone on the 75% deposited with the Central Bank plus the increased tax liabilities arising from the non-eligibility for depreciation on assets financed from the fund. It is also to be noted that the higher is the rate of inflation in the Swedish economy and the longer the period funds are "locked" in the reserve, the lower will be the benefit of channelling profits through the fund. (King and Fullerton (1984) provide a mathematical treatment of this aspect of the Swedish tax system). For a company able to take maximum advantage of the reserve fund provisions, the nominal effective tax rate is reduced from the statutory 52% to approximately 42%, to which must be added the profit sharing tax. This computation assumes an inflation rate of 9.4% (the average annual rate experienced in the Swedish economy over the period 1976-1985 (OECD 1987)) a zero "lock-in" factor, and the assumption that reserve

funds are used to finance the construction of buildings as opposed to machinery and equipment. This latter assumption is due to the fact that buildings have a longer tax life than machinery and thus maximum advantage in reducing the effective tax rate arises when reserves are used to finance buildings rather than machinery). If the lock-in period is greater than zero, the nominal effective tax rate will of course increase.

The investment reserve fund is primarily intended as a stimulant to investment in periods when the Swedish economy is in recession and in consequence unemployment is above that deemed acceptable by the Central government. The reserves are also intended to be used to stimulate investment in the designated development areas (the northern portion of the country).

Swedish company and Government officials both stated that there was a non-trivial lock-in period,i.e.-that monies deposited in the fund could not be taken out immediately. However it is very doubtful that the lock-in period in the pulp and paper industry is anywhere near a five year period. The Swedish government announced in late 1987 that it intended to introduce legislation to restrict the use of reserve funds in the pulp and paper industry to expenditures on pollution abatement. In addition, the Finance Minister announced the government intended to require all Swedish companies to place a portion of pre-tax profits into a pollution control investment reserve.

An analysis of recent annual reports of major Swedish pulp and paper companies indicates that the amount of funds held in "tax-free" reserves is small. By far the biggest item in terms of tax treatments is, as expected, the differences between "book" and accelerated depreciation allowances. King and Fullerton(1984) note that even in the 1970's, when the investment reserve fund system was widely used, less than 20% of investments were financed out of the fund.

Compulsory Investment Reserve

In 1980, the Swedish Central government made it compulsory for all companies to deposit 20% of pre-tax profits into a non-interest bearing account in the central bank, returnable if not used within 2 years. The rules governing the reserve are similar to those pertaining to the General Investment Reserve. This particular reserve is not a permanent feature of the tax system,but has been frequently invoked by the central government in recent years.

Compulsory Research and Development Reserve

The Development reserve was introduced as a temporary measure in 1985. All Swedish limited liability companies with book profits in excess of SEK 500,000 prior to tax must deposit 10% of book profits into a blocked zero interest bank account for a five year period. Monies in this account may only be used for training and education of employees or for research and development. This provision is clearly not of significant benefit to a corporation, especially given the traditionally high rates of inflation suffered by the Swedish economy.

12.6.4 Estimates of Marginal Effective Tax Rates

There is a very large body of evidence to show that the marginal effective tax rate on the Pulp and Paper industry in Canada has been significantly below both the statutory tax rate and the "average " marginal effective tax rate for manufacturing sectors. Anderson and Bonsor (1985) reported METR's for the industry based on a number of tax systems and assumed values for the Canadian vis-a-vis the U.S.$.

Assuming that an investment project is 100% equity financed (an assumption that maximizes effective tax rates compared to a project that is equity/bond financed) Anderson and Bonsor show that:

1. A company able to take full advantage of all of the available up-front tax incentives would have had a METR equal to between 9% to 13% on a major investment in kraft capacity under the pre-1982 Ontario/Canada tax system. This tax rate was lower than paid in Quebec and significantly lower than the tax rate the project would attract in the U.S.on the pre-1982 tax reform system. In the case of the U.S the METR was between 28 and 35%.

2. The 1981 US tax reform significantly increased the rate at which depreciation could be taken for tax purposes and also liberalised the ITC. For the pulp and paper industry the reform reduced the METR to around 17%. (The exact amount depends very much on the assumed level of inflation.)

3. In 1982, the Canadian Federal tax system moved to a half-year depreciation convention. In Ontario (which has not adopted this convention and also has different rules on the claiming of Depreciation compared with the federal system) the introduction of the 1982 reform caused the METR to increase to roughly the level experienced in the US

4. Both the US and Canadian corporate tax systems provided significant tax relief for the pulp and paper industry. In both countries marginal effective tax rates have been very much lower than the respective statutory rates. Prior to the introduction of the 1983 half-year depreciation convention in Canada, Canadian plants enjoyed a large advantage in tax treatments over US plants.

Further evidence that Ontario producers enjoyed a favorable tax treatment compared with US competitors is given in Daly et al (1975a). Recent tax reforms in both Canada and the US have moved in the direction of decreasing the rate at which machinery and equipment can be depreciated for tax purposes. Although this will increase the marginal effective tax rate in both countries on manufacturing investments, the overall effect will not be enormous since cuts in the rate of acceleration are accompanied by declines in the statutory federal tax rate. (Daly and Jung 1987, Grady 1986).

A comparison of marginal effective tax rates in Canada with those in force in Sweden also serve to indicate that Canadian producers have not been at a disadvantage in terms of tax treatments which Swedish producers. King and Fullerton (1984) compare marginal effective corporation tax rates for a number of sectors in Sweden, West Germany, the UK and the US In terms of the manufacturing sector, marginal effective tax rates were -under most assumptions- lower in the US than in Sweden. Daly et al (1985b), using the same methodology as King and Fullerton, have extended the analysis to include Canada. There results clearly support the position that the Canadian manufacturing sector was not at a disadvantage compared with the Swedish manufacturing sector in terms of tax treatments. The Daly et al results are reinforced by the fact that the Swedish tax environment has become somewhat tighter as a result of recent changes in tax treatments that where not simulated in their model.

In addition to the above, there is a large body of evidence which shows that the effective marginal corporate tax rate applicable to the Canadian pulp and paper sector is the lowest amongst all major industrial sectors in the Canadian economy. Daley et al (1985a) have shown that using pre-1988 tax rules, the effective marginal corporate tax rate for the overall manufacturing sector in Canada was -2.86%. For the pulp and paper sector the rate was equal to -13.87%. If the property tax is included the overall average rate for the manufacturing sector rises to 1.12%. In the case of the pulp and paper industry, the rate increases to only -10.32%. On any measure of effective tax rates, the pulp and paper industry faces

the lowest marginal effective tax rate of any major industry in the Canadian economy. Although the tax reform package of 1988 will lead to an increase in the effective marginal tax rate, the overall effect will be relatively small.

12.6.5 Subsidies

The Canadian pulp and paper industry has argued that domestic producers face "unfair" competition from heavily subsidized foreign competitors (Consultative Task Force on the Canadian Forest Products Industry (1979)). Since foreign producers compete in major markets with Canadian producers it has therefore been argued that Canadian producers must be similarly subsidized. This argument, pre-supposing for a moment that foreign producers are in fact heavily subsidized, is of very dubious value since the recipients of the subsidy will be the foreign consumers of the product. That is, if the argument that Canadian producers cannot compete in export markets with foreign producers due to the latter being heavily subsidized is correct, the granting of "countervailing" subsidies to Canadian producers represents nothing more than Canadian tax-payers being asked to subsidize non-Canadian consumers of the product.

The claim that foreign producers are heavily subsidized vis-a-vis Canadian producers is in fact a very dubious one. In recent years the Canadian pulp and paper industry has been a major recipient of government subsidies. During the period 1969-1980, the industry was the largest recipient of grants under the Federal Department of Economic Expansion's (DREE) Regional Development Incentives programme receiving 27% of the total subsidies of $671 million. Ontario firms in the forest products sector received $22 million (DREE 1980). The most significant subsidies for the Ontario industry, however, were those made under the 1979-1985 pulp and paper modernization programme. This highly controversial programme, which entailed cost-sharing agreements between the Federal government and the Provincial governments of Ontario, Quebec, New Brunswick, Nova Scotia, and Newfoundland, provided companies with mills in Eastern and Central Canada a total of $542.22 million from the Federal and Provincial governments. In Ontario producers received subsidies of $186.49 million, with $124.33 million of this being paid for by the Ontario government (Data provided by the Department of Regional and Industrial Expansion, Forest Products Directory). The largest recipient of subsidies under the Ontario portion of the programme was Great Lakes Forest Products who received $48 million. The great majority of these funds were actually received by the firms by the end of 1980. It is to be noted that one of the intentions of the subsidy programme was to provide funds for pollution abatement. An excellent analysis of this program is given by de Silva (1988) In addition to funds received under the modernization programme, companies also received subsidies under other programmes including the Forest Industry Renewable Energy Agreement, the Regional Development and Industry Programme, the Industrial Research Assistance Programme, and the Export Developments Programme.

It is clear from the above that the pulp and paper industry in Canada has been a major recipient of public funds in the form of direct subsidies. Although it difficult to provide an exact estimate of the total direct (non-tax based) subsidies received by the Ontario industry, we conservatively estimate that over the period 1975-1982 the industry received $210 million. The question then arises as to whether or not the Swedish industry has also been the recipient of major subsidies. During the period 1975-1982, the pulp and paper industry in Sweden received 4.9% of all subsidies made to industry by the Swedish government (OECD 1982, Cooke 1988). In total, this amounted to 1504 million SEK, with most of the funds being given during the "re-structuring" of the industry in the late 1970's. At exchange rates prevailing at the time of the subsidies, this is equal to approximately $350 million. In short, significantly less than the Canadian

industry received in the same period. The industry in Ontario, although very much smaller than the total Swedish industry, received in excess of $210 million over the same period.

The question of the degree to which US mills have been subsidized is a difficult question to answer. Whilst it is certainly true that the industry has not received the large subsidies that where available to mills in Canada and Sweden, it is not correct to assume that US mills have not been the recipients of subsidies. Although the US Federal government has not actively subsidized US mills, many state and local governments have made "subtle" subsidies available to mills. The most prevalent of these has been the financing of secondary treatment facilities through tax free bonds. Essentially, producers are able to finance the construction of secondary treatment facilities at a rate of interest below that which would prevail if the interest paid on the bonds were taxable. On average, the subsidy amounts to a decline in financing costs equal to a drop in interest rates of 3-5%. It should be noted that the use of tax free bonds is restricted to the financing of pollution abatement procedures which do not lead to a decline in the firms operating costs. It is difficult to estimate how many mills have received "subtle" subsidies for the construction of pollution abatement procedures. One US government official estimated that less than 25% of mills received such subsidies whereas another believed it to be less than 10%.

12.6.6 Financial Considerations

In this section we consider the supposition that Ontario producers are simply not financially able to improve effluent quality significantly and thus reduce the negative effect of kraft pulp production on the environment. The supposition implies that existing rates of return on capital earned by efficient producers are below those required to attract new capital to the industry. In consequence, tightened environmental requirements will further lower the already "un-acceptable" rate of return and hasten the exit of marginal producers.

It is not possible to provide the Ministry with a definitive and meaningful "screening" test for deciding whether or not a particular environmental requirement would place an undue and onerous burden on a mill. Apart from the practical problem of defining "undue" or "onerous", it is considered inappropriate to use industry financial ratios as a guide to profitability or fiscal capacity. Industry financial ratios are difficult to interpret at best. Fisher and Mcgowan (1983) have pointed out that accounting or financial rates of return are only useful insofar as they provide information on the underlying economic rate of return. In particular, it is to be noted that accounting rates of return are very poor indicators of ex-post profit rates over industry aggregates since they fail to allow for the rate of growth of capital investment. New large investments add disproportionately large amounts of yet to be depreciated capital to balance sheets and thus raise denominators in accounting rate of profit calculations, biasing such rates downward compared with internal rates of return. (Anderson and Bonsor 1985). There are also the very considerable difficulties involved in taking into consideration problems created by accelerated depreciation provisions. The problems are exacerbated when firms are operating in an inflationary environment.

At an industry aggregate level, there is evidence to suggest that the industry has performed relatively better than the overall manufacturing sector in the period 1962-1985. Table 12.5 compares net profits earned in the Pulp and Paper industry with those earned in manufacturing. It can be clearly seen that with the exception of the 1970-1974 period, profits in pulp and paper were in excess of those earned in the overall manufacturing sector. It is to be noted that the industry has undergone a "boom" phase since 1985 and thus can be expected to outperform the overall manufacturing sector for the period 1986-1989. de Silva (1988) provides a brief analysis of industry profitability.

Table 12.5 Net profits in the pulp and paper industry and manufacturing industries in Canada (Net profits/sales) Source: unpublished data from Statistics Canada. (de Silva 1988)

	Pulp and Paper	Manufacturing
1962-64	8.25%	4.82%
1965-69	5.65%	4.31%
1970-74	3.72%	4.22%
1974-79	4.39%	4.25%
1980-85	3.68%	3.68%

For the purposes of the Ministry, the use of industry aggregate data is likely to be misleading in a number of directions. Apart from the fact that available data is not confined to pulp mills, aggregate data essentially masks a number of underlying factors. This is especially so in Ontario when we consider that a number of the mills in the kraft sector are amongst the most profitable in North America and a number have an economic performance that can best be described as dismal.

At the company level, performance at an individual mill is rarely broken-out from the consolidated statements in published data. Nor is a mill's actual performance a reasonable indicator of whether or not effluent regulations should be tightened.

Consider the problems involved in the following example. Company "A" has had an exceptional quality of management and is highly profitable. Its plant and associated environmental control systems are in good repair and are relatively modern since the company has invested money to upgrade the capital stock. Company "B" is typified by a history of poor quality managerial decisions and inconsequence is experiencing low rates of return on capital. The Ministry orders both companies to spend $10 million on environmental projects. If the Ministry were to insist that "A" be forced to meet the new requirements and "B", because it was less efficient, not be forced to meet the new requirements, the Ministry would effectively be penalizing efficient management and what amounts to subsidizing inefficient management.

A more relevant approach is to ask whether or not an efficient mill would have difficulty in meeting the proposed regulations. In our opinion, the effluent quality requirements outlined in levels 2 and 3 in Table 11.1 do not represent an onerous burden for a company of reasonable efficiency. We point out again that all mills in the US have spent considerable amounts of money on installing secondary treatment facilities and must also bear the costs of operating such treatment facilities. In addition, mills in Sweden will, as a result of the very tight effluent regulations recently introduced by the Swedish government, be committing considerable resources to improving effluent quality. It is also relevant to point out some Ontario companies have spent considerable amounts of money on improving effluent quality and are certainly not in financial difficulty. We also note that a number of companies operating in Ontario are also operating in the US and in consequence are in fact spending considerably more on abatement procedures at US sites than at Ontario sites.

12.6.7 The Threat of Exit

It is necessary that we consider the question of whether or not some mills would have to cease production if effluent requirements were to be tightened in a non-trivial manner. In the negotiation process surrounding the writing of control orders the Ministry has, on a number of occasions, been faced with the claim that the suggested requirements would cause the firm to exit the industry.

It is logical for the industry to oppose any effluent regulation that would result in a mill having to commit resources to pollution abatement. Given that Ontario producers have little or no ability to alter the market price of pulp, committing resources to improving effluent quality will either lead to a reduction in the rate of return being earned by owners of equity investments or to lower payments to other factors of production.

It could of course be argued that Ontario producers have already benefited from those increases in market prices which have occurred as a result of tightened effluent quality requirements in other major producing regions in the world. In addition it is probable that an increase in pollution abatement requirements in other major producing jurisdictions will increase the long-run price for market pulp.

The question to be addressed is whether or not the effluent quality requirements suggested in Table 11.1 would place an undue or onerous burden on Ontario producers to the extent of rendering an Ontario location uneconomic for the production of kraft pulp. Specifically, to what extent is the threat of closing a mill in the face of the suggested effluent quality guidelines a credible one ?

A credible threat can be defined as one that the agent is believed willing and able to carry out. Consider a situation where an agent has a single mill in the province. In this case there is no strategic advantage in carrying out a threat to exit from the industry unless the costs of exit are lower than the costs involved in meeting the effluent quality requirements. In the single plant case, the threat of exit is not credible except in the situation where the cost of meeting the pollution abatement requirements increase the average variable cost of production (including the specific capital costs required on pollution abatement procedures) to a point where they are higher than the net price received by the firm. Even if this does occur, it does not necessarily mean that production will cease at the site. We offer two examples which capture the possibilities of exit in the face of a required increase in spending on environmental improvements.

Consider a case where an existing mill has dated capital equipment and is operating below minimum efficient scale (MES) and the mill is non-integrated. The average variable cost of production will be high in relation to an efficient mill of optimal scale. It is conceivable that a threat of exit in this case is real if the location itself is not an economic one for a mill of efficient scale. For example, wood costs for a mill of larger scale may be too high to allow even an efficient operator to earn an economic rate of return or indeed there may be no additional fibre available . In the long run, a plant of this nature will exit the industry in any event and thus the environmental requirements will merely accelerate exit. This does not mean that the site cannot be converted to an alternative use that is less wood intensive. **For example, a BCTMP mill of minimum efficient scale requires about a quarter of the fibre that a kraft mill of optimal scale would.** [2]

Assume a situation in which the mill is at or close to minimum efficient scale. We further specify that capital stock is of relatively recent vintage. Owing to poor productivity (either in the mill itself and/or in the

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2 Minimum efficient scale for TMP and similar mills is around 500 t/d whereas the minimum for kraft is probably over 1000 t/d

woods operation) the mill has a very high variable cost of production in relation to an efficient producer. In consequence the shut-down price for this mill will occur at a higher market price than it will for an efficient producer. Clearly if effluent quality requirements lead to an increase in the average variable cost of production, there is some price at which the firm would find it beneficial to seek exit. This result assumes that the existing owners are not capable of remedying the real cause of the problem: the high level of average variable costs. Thus the threat of an inefficient producer exiting the industry in the face of increased costs for environmental protection may have some credibility. However, it must not be assumed that the site itself is an uneconomic one. Given that the capital stock is of relatively recent vintage, the value of the plant on the market will be in excess of zero provided that a potential operator believes that he can lower the level of costs. **It must not, therefore, be assumed that simply because an existing operator cannot earn an acceptable level of profit that any other operator is in the same position. Indeed, one of the prime reasons for one company buying the assets of another is the fact that the buyer places a higher value on the assets than the seller (implying greater profits under the new management than the old).** This factor is of considerable importance in Ontario where the number of potential new sites is very limited, and thus the availability of fibre at a given site is itself an attractive feature. In addition, most Ontario mills are in reasonable to excellent condition in terms of the capital stock and thus the cost of upgrading the mill is very small in relation to the cost of constructing a new mill.

It should be argued that not relaxing the effluent guidelines in the above case is the most appropriate policy. Allowing an inefficient operator to discharge effluent of lower quality than an efficient operator has a moral hazard danger; other firms may learn that there is no penalty for being inefficient. In addition to the moral hazard argument, postponing effluent quality requirements also postpones the required improvements in factor productivity that are necessary for long term survival.

It is no secret in the industry that one Ontario kraft mill is in poor physical shape as a result of past decisions not to upgrade plant and equipment. It is clear that this particular kraft mill is close to the point where a decision must be made either to close the kraft operation or to undertake a very major investment in rebuilding and modernising the plant. Thus the future of this kraft mill is very uncertain even in the absence of the ministry requiring the company to reduce the discharges of pollutants. We point out that it would be patently incorrect to assert that a decision to close the kraft operation would be a consequence of requiring the mill to meet improved effluent quality standards.

One other operation may face difficulties in improving effluent quality. The mill is well below the size required for minimum efficient scale in a market kraft operation. In the long run, a mill of this scale may experience difficulty in surviving in a competitive market. In consequence, the requirement to improve effluent quality requirements would merely postpone the necessary restructuring of this operation. Given that fibre supply constraints in the region may well limit the probability of building a market kraft mill of minimum efficient scale, we believe it is necessary for the company to seriously consider alternatives for using the existing fibre supply. In this particular case, one of the thermo-mechanical pulping processes is an obvious candidate. Apart from the above two cases, there is absolutely no evidence to suggest that the effluent quality requirements suggested by levels II and III in Table 11.1 would impose an undue burden on mills in the province.

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14. GLOSSARY

Acute	With reference to toxicity, happening quickly, usually within 4 to 7 days for fish. Can describe an effect, or the duration of a test, e.g. an acute test. An acute effect could be a mild or sublethal one.
ADI	Acceptable Daily Intake. The amount of a substance that is considered "safe" to take into the body, on a daily basis, for a lifetime. This is almost always for humans. The value of ADI is decided by a regulatory body, after considering relevant scientific data.
Air dry	The term "Air Dry" signifies 90% dry fibre and 10% moisture (1 ADt = 900 kg OD pulp)
AOX	Adsorbable Organic Halogens. The amount of AOX measured in a sample according to a German standard test (DIN 39-409). The chlorine is the only halogen used in significant quantities in kraft pulp mills, AOX is effectively a way of determining the TOCl (q.v.) in a sample, but under different laboratory conditions. There is no precise mathematical relationship between AOX and TOCl values, but they are roughly proportional to each other, and AOX is normally the higher.
Bioaccumulation	A general term, meaning that an organism stores within its body, a higher concentration of a substance than is found in the environment. This is not necessarily harmful. For example, freshwater fish must bioaccumulate common salt if they are to live. Many toxicants, such as arsenic, can be handled and excreted by aquatic organisms, so that they are not included among the dangerous bioaccumulative substances.
Bioassay	This term can be used for toxicity tests with fish, but it is probably best to reserve it for the formalised procedures used in testing the potency of drugs (pharmaceuticals).
Bioconcentration	Accumulation of a chemical directly from the water, to a higher concentration in an aquatic organism. The bioconcentration results from simultaneous processes of uptake and elimination.
Bioconcentration factor	(BCF) The concentration of a specific chemical in an aquatic organism, divided by the concentration of the chemical in the water in which the organism has been living. BCF is usually determined experimentally. Dangerous bioaccumulative toxicants would usually have BCF's with values in the thousands or tens of thousands
BCTMP	Bleached Chemi-Thermomechanical Pulp.
BK, BKM, BKME.	Abbreviations for Bleached Kraft, Bleached Kraft Mill, and Bleached Kraft Mill Effluent. All referring to a pulp mill the operates by kraft or sulfate process, and bleaches some or all of the product.

Black Liquor	A liquid in the kraft process, composed of spent pulping chemicals and wood residues. Weak black liquor refers to concentrations under 20% solids, strong black liquor to concentrations over 50% solids.
Blow Tank	A tank which receives the pulp discharged (blown) from the digester in a chemical pulp mill
BOD	Biochemical Oxygen Demand is a property of water or wastewater, determined by measuring the quantity of oxygen consumed by a sample under controlled conditions (20°C, neutral pH) for a defined time period. The most commonly used period is 5 days which is sometimes written as BOD_5. The use of "BOD" for the 5-day test is common in North America and has been adopted in this report. BOD is expressed as mg/L ("parts per million"), the same unit as is customary for dissolved oxygen, or simply as a weight, as in "kg of BOD per tonne of pulp".
Bone Dry(BD)	See Oven Dry
Brightness	A measure of the whiteness of paper as compared to a standard . Refer also to discussion in Section 3.3.1
Brown Stock	Kraft slush pulp prior to bleaching
Carcinogenic	Capable of causing cancer.
Caustic	Commonly used name for sodium hydroxide
Caustic Extraction	Bleaching stage where highly coloured organics are dissolved with alkali, normally NaOH
Causticiser	A tank used to allow calcium hydroxide and sodium carbonate to react and form sodium hydroxide and calcium carbonate.
Chronic	Long-lasting or continued. Can refer to the effect or the duration of exposure. In mammalian toxicology, usually signifies exposures lasting at least one-tenth of a lifetime. In aquatic toxicology, is sometimes used to mean a full life-cycle test.
COD	Chemical Oxygen Demand. A similar concept to BOD, except that the measurement of amount of oxygen consumed is based on rapid chemical oxidation of the sample. BOD and COD are generally poorly correlated.
Condensate	Water condensed from steam which has come into contact with a surface at a lower temperature during a process. Contaminated or foul condensate usually refers to a condensed vapor from evaporation of black liquor or other spent pulping liquor.
Coniferous Trees	Cone-bearing and evergreen trees, such as spruce, hemlock, Douglas fir, pine.
Consistency	Weight per cent of moisture free, or air dry (as specified) fibres in a suspension of pulp fibres in water.

Cook	Normal term for the chemical pulping process in the digester where the fibre is separated from lignin by chemicals under pressure, at elevated temperatures as described in the pulping process section of the manual.
Decanter (turpentine)	A tank used to separate turpentine from condensate.
Deciduous trees	Hardwoods or broadleaf trees which lose their leaves in winter, such as alder, maple, oak, birch, cottonwood.
Decker	An apparatus for dewatering pulp by filtering the fibres out on a mesh covered drum. It generally consists of a vat, a cylinder mold and a couch roll from which stock is removed by a doctor.
DO	Dissolved oxygen, normally measured in milligrams/litre and widely used as a criterion of receiving water quality.
EC50	Median effective concentration. As LC50, except that it may apply to any effect, lethal or non-lethal. The effect as well as the exposure-time must be specified.
Ecosystem	An interacting system of all living organisms in a circumscribed region of similar characteristics, and the non-living substrate, nutrients, energy, and other environmental components.
Effluent	A waste material discharged into the environment. In this report, the effluent refers to the liquid waste with its suspended materials, which is discharged into surface waters.
Effluent standard	A regulation concerning the quality of a liquid waste, or the concentrations of substances that it may contain. This standard applies "at the end of the pipe".
Eutrophic	The condition of a lake or other waterbody which has high productivity because fo the high levels of nutrients in the water. Such a lake would have blooms af algae and problems of low oxygen in deep waters because of decomposition of organic matter. Lake Erie reached that status in the 1970's but has generally improved to a mesotrophic status as inputs of nutrients have been reduced.
Fillers	Materials used to fill voids which occur between fibres. Most printing paper except newsprint contains substantial amount of filler. The term is also used for some interior, low grade fibre layers in multiple ply board.
Filter	A device used to separate suspended solids from a liquid.
Filtrate	The liquid that passes through a filter. In kraft pulp processing filtrate is usually either white water, black liquor or lime mud washings.
Furnish	The specific mixture of raw materials, both pulp and chemicals, from which a particular grade is manufactured, ready to be delivered to the paper machine.

Genotoxic	Damaging the inherited genetic material of a living organism, i.e. the genes and their component DNA.
Green Liquor	A liquid in the kraft process composed of the chemicals obtained from the recovery furnace. Primarily sodium sulphide and sodium carbonate in aqueous solutions.
Grits	In kraft mills, the inert lime rejected from the slaker in the recausticising department.
Groundwood	Pulp produced by mechanically defibering wood with revolving grindstone and refining plates. See also "Refiner Groundwood"
Hemicellulose	Portion of wood fibre consisting of sugar-like substances intimately associated with cellulose in the fibre wall and removed mainly in the cooking process.
Hog Fuel	Term for wood waste fuel widely used in pulp and paper industry boilers. It includes some of the following: bark; sawdust; reject chips; sticks; branches; cutoffs and other saw mill and wood harvesting wastes. The major component is usually bark.
Hurdle Cost of Capital	The rate of return which is required by private (non-governmental) investors before they will undertake a capital investment.
Kappa number	A measure of lignin in pulp, according to a standard laboratory procedure. Widely used as a tool for control of mill operations. Bleachable grades of unbleached kraft pulp generally have a Kappa number from 5 to 35, depending on the wood species and the extent of delignification.
Knotter	A type of screening equipment used to separate knots and other large, oversized and unwanted material from wood pulp.
KM, KME	Kraft mill and kraft mill effluent. See BK.
Kraft Pulp	Pulp produced by the kraft process (see pulping process in Section 3.2). Also known as sulphate pulp.
LC50	Median lethal concentration. The concentration of a substance that is estimated to kill half of a group of organisms. The duration of exposure must be specified (e.g. 96-hour LC50).
Lethal	Causing death, or sufficient to cause death.
Life-cycle test	With aquatic organisms, a test in which exposure generally starts with newly-hatched stages and continues at least until they reproduce. Usually, the second generation receives continuing exposure, and is studied for a month (fish).
LOEC	The lowest observed effect-concentration. The lowest concentration that causes a significant adverse effect in a sublethal test.

Machine Dry	The degree of dryness of pulp, or more commonly paper, as it leaves the drying machine.
Machine Finish (MF)	The normal finish applied to the paper machine equipped with conventional dryers (differentiated from a Yankee dryer).
Market Pulp	Pulp products such as kraft bleached softwood pulp sold to customers outside the producing company for machine furnish.
Mesotrophic	The condition of a lake which is moderately productive as a result of moderate concentrations of nutrients.
mg/L	Milligrams of the substance in question, contained in one litre of solution. Roughly speaking, parts per million. This is the common unit for assessing water quality.
Mutagen	A chemical that causes an alteration of the inherited genetic material, i.e. the DNA of the genes. In the narrow sense, the chemical alters the genetic material of paternal or maternal sex cells.
NCG	Non-condensable gases are gases emitted from several parts of the kraft pulping process which do not condense in the commonly installed condensing equipment. TRS and/or methanol are the predominant components.
NPOX	Non-Purgeable Organic Halogen (See also AOX, POX)
NOEC	The no-observed-effect concentration. The highest concentration in a sublethal test that does not cause a significant adverse effect, in comparison to the controls. Also called NOAEC, the no-observed adverse effect concentration.
NOEL	No observed effect level
Oligotrophic	The condition of a lake which has low productivity because of lack of nutrients. The water would be clear. Lake Superior is oligotrophic.
Organochlorine	An organic compound which includes chemically bound chlorine. Many organochlorines are formed in the kraft bleaching process whenever chlorine or chlorine based compounds are used. Thousands of chlorinated organic compounds exist, but only a small proportion of those in kraft mill effluent have been identified. TOCl is one of many ways of measuring organochlorines, but this is expressed as the weight of organically bound chlorine,not the weight of organochlorine molecules.
Oven Dry (OD)	Pulp or paper dried in an oven by a standard laboratory procedure to the point where it contains no moisture. The term Bone Dry (BD) is commonly used synonymously. Oven dry weight divided by 0.9 equals the air dry weight, in standard practice.

Oxidation Efficiency	(As applied to kraft black liquor) Percentage reduction of sodium sulphide concentration in the black liquor after it has been oxidised by blowing air or oxygen through the liquor, as applied to black liquor oxidation processes.
Particulate Emissions	Generally, this consists of all solid material discharged from a stack or vent. Specifically the particulate flow is defined by a standard test method.Particulate emissions are usually expressed as mg/m^3
pH	A measure of the acid or alkaline nature of water or some other medium. Specifically, pH is the negative logarithm of the hydronium ion concentration (H_3O^+). Practically, pH 7 represents a neutral condition in which the acid hydrogen ions balance the alkaline hydroxide ions. Values of pH below 7 represent acid conditions and values above 7 are alkaline. A change of one unit, for example from 7 to 6, represents a ten fold increase in hydrogen ion activity, and thus a ten fold increase in the "acidic" nature of a water. Soft northern waters would typically range from pH 6 to 7.5; hard waters of southern Ontario would usually be close to pH 8. The pH of the water can have an important influence on the toxicity of chemicals in kraft pulp mill effluents.
Pollution	With reference to water pollution, the addition of something to the water by humans, resulting in a measurable effect, which is deleterious to some use of the water by living organisms including humans.
POX	Purgeable Organic Halogen (see also AOX, NPOX)
Precipitator (Electrostatic)	A piece of equipment use to recover solids from a gas stream by the use of high voltage applied to plates or wires in the stream by the use of electrostatic forces.
Pretreatment	Describes initial treatment processes before an effluent reaches primary treatment. The processes are designed to remove grit, coarse material and debris, to neutralise acid or alkaline wastes, to equalise the effluent characteristics and flows by mixing the collected effluent streams and directing occasional large flows or concentrated streams which are a normal part of pulp mill operations to spill tanks or basins.
Primary treatment	This is intended to remove suspended solids from the effluent and normally includes dewatering the recovered settled solids or sludge to facilitate disposal to landfill or combustion process. Primary treatment is a pre-requisite for most secondary treatment processes.
Recovery Furnace	A unit used to burn recovered cooking liquor to produce stream and to reprocess cooking chemicals. Frequently known as the recovery boiler. Refer to Section 3.4
Saveall	Equipment used to recover fibres and filler from the white water. Usually a wire-covered rotating drum or wire-covered discs. Vacuum is employed to draw the water through the wire. Today, the "wires" are usually plastic. There are several other types of save-alls working on a sedimentation or flotation principle.

Screen Room	A common term for the screening and cleaning department which usually follows a pulping operation.
Scrubber	A piece of equipment used to remove certain gases or solids from a gas stream utilising a spray of liquid, usually water or an aqueous solution of reactant.
Secondary treatment	A stage o waste treatment in which micro-organisms decompose organic constituents in the effluent. In the process, they use oxygen for their metabolism and to oxidise the waste material. Most secondary treatment processes also reduce toxicity.
Shives	A small bundle of fibres that has not been separated completely in the pulping operation.
Shrinkage	Term normally applied to the pulp loss in bleaching due to removal of lignin. Usually expressed as percent. Pulp typically shrinks about 7% on bleaching.
Sludge Filter	A piece of equipment used to concentrate suspended solids recovered from an effluent by clarifier.
Smelt	The organic chemicals that are obtain in molten form from the recovery furnace.
Soda Loss	The loss of sodium salt due to imperfect washing of the pulp, or in the recovery of sodium compound in the chemical recovery system.
Stock	A general term for suspension of pulp fibre in water, usually implies a consistency between 0.2% and 15%. A papermaker's terms for the beaten, refined and mixed materials (furnish) in a water suspension as supplied to the paper machine (also called "stuff")
Stock Preparation	A term for the operation which occur between pulping or bleaching and formation of the web on the paper machine operations which may include blending of several pulps, addition of colour, filler and other materials and chemicals.
Sublethal	A concentration or level that would not cause death. An effect that is not directly lethal.
Sublethal Toxicity	See Toxicity
Sulphate Pulp	A term used often for kraft pulp, especially in Scandinavian literature.
Sulphidity	In white liquor, the percentage of sodium sulphide to sodium sulphide plus sodium hydroxide where all compounds are expressed as sodium oxide.
Suspended solids	Particles of matter suspended in the water. Measured as the oven dry weight of the solids, in mg/L, after filtration through a standard filter paper. Less than 25 mg/L would be considered clean water, while an extremely muddy river might have about 200 mg/L of suspended solids.

Teratogen	A substance that causes alteration in the developing cells, tissues, or organs at the embryonic stage of development.
Tertiary treatment	This is a final process of effluent treatment after primary and secondary treatment steps. It embraces a broad range of processes used to remove items such as colour, odour, taste, and toxicity.. It is often used for removing nutrients, especially phosphorus, from municipal effluents.
TOCl	Total Organically bound Chlorine. Quantity of organically bound chlorine in a sample, determined according to method described by Sjostrom (1982). This is similar to the measurement of AOX, except that the TOCl is sorbed onto XAD (ion-exchange resin), instead of activated carbon. This is a measure of the total chlorine in organic compounds, many of which may be unidentified.
TOX	Abbreviation commonly used to refer to the Total Organic Halogen analytical procedure defined by APHA et al. (1985). This procedure is used in North America for determination of organically bound halogens in pulp mill process streams and wastewaters.
Toxic	Descriptor of a substance, a dose, or a concentration that is harmful to a living organism.
Toxicity test	Any test in which the harmful action of a substance is measured by observing the effect it has on a living organism, or organisms.
TRS	Total Reduced Sulphur. A general term for sulphur gases emitted from the kraft process, excluding sulphur dioxide and trioxide. Generally considered to include hydrogen sulphide, dimethyl sulphide, dimethyl disulphide and methyl mercaptan. These gases are the principal cause of the classic kraft mill odour. They are generated by the reaction of sodium sulphide with some of the wood components. TRS is normally expressed as elemental sulphur.
ug/L	Micrograms per litre. Roughly speaking, a part per billion, or only one-thousandth of the strength of one mg/L.
VSD	Virtually safe dose. A daily intake, continued for a lifetime, that is estimated to have very little risk of causing disease or toxic effect. Almost always refers to humans, and usually involves a risk of one in a million.
Water quality criterion	(Plural: criteria.) In the broad sense, a criterion is a number which may be used for judgement. In aquatic toxicology, w.q.c. commonly means the highest concentration which is not expected to cause an appreciable effect on an aquatic system or its users. The number is derived from available scientific data. There may be several sets of criteria for the same substance, e.g. for drinking water, industrial use, etc. These criteria always apply after dilution in the receiving water.
Water quality objective	Similar to water quality standard except that it is merely an expression of a desirable goal, and does not have the same force as a regulation, nor is there a penalty for transgression.

Water quality standard	A maximum concentration of a pollutant, or a maximum or minimum level of some characteristic such as pH, which is not to be transgressed in a body of water. These numbers are promulgated by a government or its agency by means of laws or regulations. They may or may not adhere closely to criteria.
White Liquor	A liquid in the kraft process composed of the chemicals used in the digester to cook the wood chips. Primarily sodium sulphide and sodium hydroxide in aqueous solution.
White Water	Abbreviated WW, a general term for water removed from a pulp suspension and containing a small amount of fibre and/or additives. On a paper machine, the excess water drained through the wire from the furnish. The use of the term "white water" usually implies low dissolved solids content. Always white when white paper is produced, it contains pigments when coloured paper is being made, and can be any colour.

15 CONVERSION FACTORS

1 kg (kilogram)	= 2.2046 pounds (lb.)	[lb x 0.4536 = kg]
1 t (tonne)	= 1.102 short tons	[s. tons x 0.9072 = tonnes]
	= 0.9842 long tons	[l. tons x 1.016 = tonnes]
1 ADt	= 0.9 oven dry tonnes pulp	
1 m (metre)	= 3.281 feet	[feet x 0.3048 = m]
1 km (kilometre)	= 0.6214 miles	[miles x 1.609 = km]
1 hectare	= 2.471 acres	[acres x 0.4047 = hectares]
1 km^2	= 100 hectares	
1 km^2	= 0.3861 square miles	[sq. mi. x 2.590 = km^2]
1 L (litre) of water	= approx. 1 kg	
1 m^3 of water	= 1000 L	= approx. 1 tonne
	= 35.31 cubic feet	[cubic feet x 0.02832 = m^3]
	= 220.0 Imp. gal.	[Imp. gal. x 0.004546 = m^3]
	= 264.2 U.S. gal.	[U.S. gal. x 0.003785 = m^3]
1 m^3/t	= 199.6 Imp. gal./short ton	[1000 gal/ton x 5.011 = m^3/t]
	= 239.7 U.S. gal./short ton	[1000 gal/ton x 4.171 = m^3/t]
1 kg/tonne	= 2 lb/short ton	[lb/ton x 0.5000 = kg/t]

Fractional Units

1 t (metric tonne)	= 10^6 g	= 1000 kg (kilogram)
1 kg	= 10^3 g	= 1000 g (gram)
1 g	= 1 g	= 1000 mg (milligram)
1 mg	= 10^{-3} g	= 1000 ug (microgram)
1 ug	= 10^{-6} g	= 1000 ng (nanogram)
1 ng	= 10^{-9} g	= 1000 pg (picogram)
1 pg	= 10^{-12} g	= 1000 fg (femtogram)
1 fg	= 10^{-15} g	= 1000 ag (attogram)
1 ag	= 10^{-18} g	

Approximate Equivalents

1 g/L	= 1 g/kg	= 10^{-3} g/g	= "1 part per thousand"
1 mg/L	= 1 mg/kg	= 10^{-6} g/g	= "1 part per million"
1 ug/L	= 1 ug/kg	= 10^{-9} g/g	= "1 part per billion"
1 ng/L	= 1 ng/kg	= 10^{-12} g/g	= "1 part per trillion"
1 pg/L	= 1 pg/kg	= 10^{-15} g/g	= "1 part per quadrillion"